THE UNIVERSITY OF ALBERTA

ESTIMATION OF PARAMETERS IN ORDINARY DIFFERENTIAL EQUATIONS USING INTEGRAL FUNCTIONS

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA

FALL, 1973

ABSTRACT

Given a model which consists of a system of differential equations describing a certain physical phenomenon, a study has been made of the problem of estimating the unknown parameters in the model from experimental data. In such problems, the integration of the differential equations describing the process and sensitivity coefficients is the most time consuming part. An attempt has been made to reduce the time requirements by introducing into the original model approximating functions of some kind. The resulting expressions do not require one-step or multi-step integration methods which are time consuming.

It has been assumed that the only errors involved are those in the observations, and no dynamic disturbances are present in the system.

Three problems have been studied; the first one is a boundary value problem and the last two are initial value problems. As mentioned earlier, the original model in each problem consists of a system of differential equations. Once this system has been transformed to a system of integral equations, functions approximating the observed variables in terms of the independent variable have been introduced. In the first two problems, the systems of differential equations have been integrated using the Green's function approach.

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Given a model which consists of a system of differential equations describing a certain physical phenomenon, a study has been made of the problem of estimating the unknown parameters in the model from experimental data. In such problems, the integration of the differential equations describing the process and sensitivity coefficients is the most time consuming part. An attempt has been made to reduce the time requirements by introducing into the original model approximating functions of some kind. The resulting expressions do not require one-step or multi-step integration methods which are time consuming.

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The resulting expressions have been integrated analytically. In the third problem, which represents a more general case, where analytical integration is not possible, use of simple integration scheme, such as the trapezoidal rule has been made.

The main problem associated with the approach employed, as will be seen, lies in the difficulties encountered in establishing proper confidence intervals for the parameter estimates.

ACKNOWLEDGEMENTS

The author wishes to thank his thesis supervisor, Dr. D. Quon, for his guidance and constructive criticisms during the course of the work.

The assistance of the Data Acquisition, Control, and Simulation Center (DACS) staff is also gratefully acknowledged.

Special thanks go to Miss Susan Schultz for typing the thesis.

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CHAPTER I

INTRODUCTION

Finding a mathematical model which will describe a certain process, be it separation, chemical reaction, or a transport process, has been of growing concern in the field of chemical engineering. Sometimes the mechanism of the process is partially understood and an empirical relationship is used to describe it. Sometimes complete understanding of the mechanism is possible, with the resultant mathematical model available. In both cases, complete information about the model is possible only by estimating the unknown parameters in it, based on observing the system behavior. The observations are usually made at discrete points, although in the case where time is the independent variable, one has additional access to continuous observations. The estimation schemes to be reviewed below are non-sequential in nature, i.e., they apply to the case where estimation is done subsequent to observations. Particular references to kinetic studies will also be made.

A. Literature Survey

Until recently, kinetic analysis of systems linearized by appropriate transformations have been common. These

approaches suffer two major drawbacks. First, they cannot represent real systems encountered in many situations, which are non-linear in nature, and second, under transformations, there is no guarantee that the original error distribution which has been judged appropriate will be preserved. The availability of modern computers, on the other hand, has made the analysis of non-linear systems feasible.

Examples for using analytical integration methods prior to estimation are given by Levenspiel (20), Wright (32), and Kittrell, Mezaki, and Watson (15). For simple systems one cannot object to this approach. However, it should be kept in mind that, although some systems will lend themselves to analytical integration, the resulting models to be used for estimation are rather complicated to work with. The three-component, monomolecular, reversible reaction system analyzed in Chapter IV can be cited as an example.

The general concept behind the estimation procedures is discussed by Bard and Lapidus (1), Quon (25), and Nieman, Fisher, and Seborg (23). They can be classified into three main groups; least-squares, maximum likelihood, and Bayesian estimation. The first, merely requires the assumption of zero expected value of the observation errors. The second, assumes a distribution for the observation errors, usually the normal distribution. The weights, which express one's confidence in the observations of different variables, are considered to be part of the system and estimated together with the parameters. The third method takes into account the existing

information about the parameters prior to the experiment. It is particularly useful for sequential experimentation.

So far, only the existing criteria for estimation have been mentioned. An equally important aspect of estimation is the computational scheme employed to satisfy the criteria mentioned in the preceding paragraph. To this end, consider the initial value problem described by:

$$y' = f(y,x:\underline{a}) \tag{I-1}$$

$$y(x_0) = y_0 \tag{I-2}$$

where y = observed dependent variable,

x = independent variable,

$\underline{a}$ = p-vector of unknown parameters.

The prime stands for the derivative of y with respect to x.

One could, as mentioned earlier, integrate Equation (I-1) analytically, if possible, and choose the resulting equation as a model:

$$y = g(x:\underline{a}) \tag{I-3}$$

The alternative would be to work directly with the model given by Equation (I-1). In any case, the estimation procedures to be outlined below are the same, regardless of the model being used. The only difference is that numerical integration might be necessary if one is working with the

model given by Equation (I-1).

The existing computational methods can be divided into two main classes; direct search methods and gradient methods. Usually, direct search methods are used to provide an approximation as a starting point for the gradient methods which are iterative in nature.

All the gradient methods provide a correction $\underline{\delta}$ to the parameter estimates at the iteration stage under question, using:

$$\underline{\delta} = - \lambda \underline{R} \underline{v} \qquad \text{(I-4)}$$

where λ = a scaler determining step length,

$\underline{v} = \{\frac{\partial S}{\partial a_j}; j=1,2,\ldots,p\}$

S = objective function to be minimized, a function of $\underline{\varepsilon}^T \underline{\varepsilon}$,

$\underline{\varepsilon} = \tilde{\underline{y}} - \hat{\underline{y}}$,

$\tilde{\underline{y}}$ = N vector of observed values of y,

$\hat{\underline{y}}$ = N vector of predicted values of y by the algorithm,

N = number of observation points.

The different forms of the gradient method emerge as a result of the choice of λ and $\underline{R}$. This point has been discussed by Bard and Lapidus (1) in detail. One of the most commonly used approaches is to express $\underline{R}$ in terms of the sensitivity coefficients which are the partial derivatives

of the dependent variables with respect to the parameters. In the case where the model given by Equation (I-1) is used, this requires numerical integration. An alternative method is to evaluate them by differences, using slightly perturbed parameter values. It should be pointed out that the computational requirements are the same in both cases.

Quasilinearization has received considerable attention (2, 9, 12, 17). This method converts the non-linear initial or boundary value problem into a series of linear initial value problems. Donnelly and Quon (9) have reduced the number of equations to be integrated by considering the structure of the equation.

Hwang and Seinfeld (12) have shown that a gradient technique similar to the one summarized by Equation (I-4) can be developed using the notions of quasilinearization. In this case, $\underline{R} = (\underline{G}^T\underline{G})^{-1}$, and $\underline{v} = \underline{G}^T\underline{\varepsilon}$, in specific, where $\underline{G}$ is the matrix of sensitivity coefficients.

One of the shortcomings of the quasilinearization approach is that the convergence cannot be guaranteed. To assure convergence, Donnelly and Quon (9) have perturbed the observed data to generate a new set of data which will fall in the region between the observed data and that predicted by the algorithm. Seinfeld and Gavalas (26) recommend the use of polynomial fitting to the first several data points, or the use of the steepest descent algorithm for the initial stages of calculation.

Invariant imbedding (8, 17) also appears as a powerful

tool in estimation. Optimal control concepts are applied in the minimization of the objective function over the whole trajectory. This method is sequential in nature, i.e., after each data point is taken, a new set of states and parameter estimates is obtained.

The use of expansion functions in the solution of differential equations is quite common (6, 16). They have been also used in the reverse problem of identification (27, 28).

The approach in this work will utilize expansion functions in estimating constant parameters in systems which have already been identified and can be represented by a system of ordinary differential equations. Cresswell and Quon (6) have proposed a method for attacking a problem which has also been considered in Chapter III. Lee (18) has used expansion functions in determining parameters which are functions of the independent variable x.

Without a passing reference to the methods stressing the design of sequential experiments the review would not be complete. A number of papers have been published in this field (3, 4, 14, 22). It is generally recommended that the experiment be run under conditions where the determinant of $\underline{G}^T\underline{G}$ is maximized, where $\underline{G}$ is the matrix of sensitivity coefficients. The parameter estimates obtained from the last experiment are used in evaluating the new determinant of $\underline{G}^T\underline{G}$ over a grid of experimental conditions to choose the most favorable ones. Box and Lucas (4) have shown that under

certain assumptions this choice is equivalent to minimizing the volume of the joint confidence region of the parameters.

B. Objectives of the Study

The main drawbacks of the gradient methods and the quasilinearization and invariant imbedding algorithms outlined in Section A is the time requirements for the numerical integration of the differential equations describing the system and sensitivity coefficients.

As pointed out in the previous section, the use of analytical integration methods is limited, even if analytical integration is possible.

The main effort in this work is spent in combining the features of the gradient and analytical integration methods in a way which will reduce the computation time requirements. To this end, approximating functions, depending on the nature of the problem at hand are used. In some cases, it is necessary to specify these functions completely (i.e., estimate the coefficients involved) prior to the estimation of the parameters of original interest. In other cases it is possible to estimate both parameter sets simultaneously. The problems studied in Chapters III and IV enjoy the property that the system of differential equations can be put into a self-adjoint form. In cases where this does not prove applicable (Chapter V) a more general approach is taken.

In this work, it is assumed that the model describing the system is already available. It is further assumed

that no dynamic noise is present in the system. Thus, the errors are limited to those in the observations.

CHAPTER II

THEORY

Consider the initial value problem[1]

$$y''(x) + u(x:\underline{a})y'(x) = f(y(x),v(x:\underline{a}),x) \qquad \text{(II-1)}$$

$$y(x_0) = \nu \qquad \text{(II-2)}$$

$$y'(x_0) = \eta \qquad \text{(II-3)}$$

where the prime denotes the derivative of y with respect to x, the independent variable; $\underline{a}$ is a p-vector of unknown parameters. The general solution of Equations (II-1) to (II-3) is:

$$y(x) = \int_{x_0}^{x} F(x,\xi:\underline{a})f(y(\xi),v(\xi:\underline{a}),\xi)p(\xi:\underline{a})d\xi + z(\nu,\eta,x:\underline{a}) \qquad \text{(II-4)}$$

where

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[1] For simplicity of notation, only the case with one dependent variable is considered. The above treatment can be generalized without any difficulty to handle cases where there are more than one dependent variable.

$$p(x:\underline{a}) = \exp\left[\int_{x_0}^{x} u(\xi:\underline{a})d\xi\right] \qquad \text{(II-5)}$$

In Equation (II-4) the term $z(\nu,\eta,x:\underline{a})$ accounts for the initial conditions, so that Equations (II-2) and (II-3) will be satisfied. The procedure for determining $F(x,\xi:\underline{a})$ is given in (31).

Now consider the boundary value problem

$$y''(x) + u(x:\underline{a})y'(x) = - f(y(x),v(x:\underline{a}),x) \qquad \text{(II-6)}$$

$$- \mu_1 y'(x_0) + \rho_1 y(x_0) = r \qquad \text{(II-7)}$$

$$\mu_2 y'(x_f) + \rho_2 y(x_f) = s \qquad \text{(II-8)}$$

The general solution of Equations (II-6) to (II-8) is:

$$y(x) = \int_{x_0}^{x_f} G(x,\xi:\underline{a})f(y(\xi),v(\xi:\underline{a}),\xi)p(\xi:\underline{a})d\xi$$

$$+ \frac{p(x_0:\underline{a})}{\mu_1} r\, G(x,x_0:\underline{a}) + \frac{p(x_f:\underline{a})}{\mu_2} s\, G(x,x_f:\underline{a}) \qquad \text{(II-9)}$$

where $p(x:\underline{a})$ is again given by Equation (II-5). The procedure for determining $G(x,\xi:\underline{a})$ is given in (31).

If $\mu_1 = 0$, $\frac{1}{\mu_1} G(x,x_0:\underline{a})$ should be replaced by $\frac{1}{\rho_1} \frac{\partial G}{\partial \xi}(x,x_0:\underline{a})$. If $\mu_2 = 0$, $\frac{1}{\mu_2} G(x_1,x_f:\underline{a})$ should be replaced

by $-\frac{1}{\rho_2}\frac{\partial G}{\partial \xi}(x,x_f:\underline{a})$.

The general solution of

$$y'(x) + u(x:\underline{a})y(x) = f(y(x),v(x:\underline{a}),x) \qquad \text{(II-10)}$$

$$y(x_0) = \nu \qquad \text{(II-11)}$$

is given by

$$y(x) = p(x:\underline{a})^{-1}\int_{x_0}^{x} p(\xi:\underline{a})f(y(\xi),v(\xi:\underline{a}),\xi)d\xi + \nu \qquad \text{(II-12)}$$

Now assume that a set of observations $\{\tilde{y}_i,x_i;$ $i=1,2,\ldots,N\}$ is available. On the basis of those observations, the estimation of $\underline{a}$ is desired. Suppose one replaces $y(x)$ by using an approximating function of some kind:

$$y(x) \tilde{=} \phi(x:\underline{b}) \qquad \text{(II-13)}$$

where $\phi(x:\underline{b})$ is the approximating function, and $\underline{b}$ is the q-vector of parameters in it. Replacing $y(\xi)$ on the right-hand side of either Equation (II-4), (II-9), or (II-12), depending on the problem at hand, by $\phi(\xi:\underline{b})$ gives:

$$y(x) \tilde{=} \psi(x:\underline{a},\underline{b}) \qquad \text{(II-14)}$$

Replacing $y(x)$ in Equation (II-14) by the observed values, one obtains the following error model:

$$\varepsilon_i = \tilde{y}_i - \psi(x_i:\underline{a},\underline{b}); \quad i=1,2,\ldots,N \tag{II-15}$$

Now the problem has been reduced to the estimation of $\underline{a}$ and $\underline{b}$ such that the least-squares objective function

$$S = \sum_{i=1}^{N} \varepsilon_i^2 \tag{II-16}$$

is minimized. It should be noted that, in some cases, due to the structure of the equations, the interaction between the components of $\underline{a}$ and $\underline{b}$ cannot be avoided, so that their simultaneous estimation is not possible. One could, then, define a new error model of the form:

$$\varepsilon_i = \tilde{y}_i - \psi(x_i:\underline{c}); \quad i-1,2,\ldots,N \tag{II-17}$$

where $\underline{c}$ is a vector with a dimension smaller than p+q, whose components have been obtained by lumping the components of $\underline{a}$ and $\underline{b}$. Depending on the situation at hand, $\underline{c}$ could still retain some of the elements of $\underline{a}$. After estimating $\underline{c}$ using least-squares, application of a second least-squares procedure would give the desired estimates of $\underline{a}$ and $\underline{b}$.

Another approach would be to estimate $\underline{b}$ originally, using the following error model:

$$\varepsilon_i = \tilde{y}_i - \phi(x_i:\underline{b}); \quad i=1,2,\ldots,N \tag{II-18}$$

Using $\hat{\underline{b}}$, the estimate of $\underline{b}$, the following error model would

be used to estimate $\underline{a}$:

$$\varepsilon_i = \tilde{y}_i - \psi(x_i:\underline{a},\hat{\underline{b}}); \quad i=1,2,\ldots,N \tag{II-19}$$

If possible, the use of a two-stage estimation procedure should be avoided, since the estimates of $\underline{a}$ will somewhat be dependent on the estimates of $\underline{b}$.

Note that the approach discussed so far has been based on the assumptions that the differential equation can be converted into a self-adjoint form, and the analytical integral of

$$\int_{x_0}^{x} u(\xi:\underline{a})d\xi$$

exists. It has also been assumed that an analytical expression for $F(x,\xi:\underline{a})$ or $G(x,\xi:\underline{a})$ can be found. When these assumptions hold, the above approach is particularly appealing, since it lends itself to analytical integration. When these assumptions do not hold, one would have to resort to a more general approach. To this end, consider the initial value problem:

$$y'(x) = h(y(x),x:\underline{a}) \tag{II-20}$$

$$y(x_0) = \nu \tag{II-21}$$

Again, a set of observations $\{\tilde{y}_i, x_i;\ i=1,2,\ldots,N\}$ is available. Integrating Equation (II-20) gives:

$$y(x) = \nu + \int_{x_0}^{x} h(y(\xi),\xi:\underline{a})d\xi \qquad \text{(II-22)}$$

Now assumed that $y(x)$ is replaced by an approximating function whose parameters have already been estimated:

$$y(x) \tilde{=} \phi(x:\hat{\underline{b}}) \qquad \text{(II-23)}$$

Replacing $y(\xi)$ in the integrand of Equation (II-22) by $\phi(\xi:\hat{\underline{b}})$ gives:

$$y(x) \tilde{=} \nu + \int_{x_0}^{x} h(\phi(\xi:\hat{\underline{b}}),\xi:\underline{a})d\xi \qquad \text{(II-24)}$$

Replacing $y(x)$ in Equation (II-24) by the observed values gives the following error model:

$$\varepsilon(x) = \phi(x:\hat{\underline{b}}) - \nu - \int_{x_0}^{x} h(\phi(\xi,\hat{\underline{b}}),\xi:\underline{a})d\xi \qquad \text{(II-25)}$$

The above error model is continuous in x; hence, it can be evaluated at as many points as desired.

Note the basic difference between the conventional estimation methods and the above approach. In the former, the differential equations describing the system and sensitivity coefficients are integrated using one-step or multi-step formulas. The step size used in integration plays an import-

ant role in the stability of the solution of these differential equations. Thus integration should be carried out using fairly small increments of x. With the new approach, on the other hand, the integrand can be evaluated at a certain number of x points throughout the interval, and a quadrature formula, or a simpler formula such as the trapezoidal rule, or Simpson's rule can be used for integration. The number of points at which the integrands are evaluated could thus be reduced considerably, since the integrals would not be as sensitive to the step size used.

A brief outline of the non-linear least-squares procedure employed is given in the Appendix.

CHAPTER III

A NONIDEAL FLOW CHEMICAL REACTION PROBLEM

A. Statement of the Problem

Consider the differential equation describing the composition of a single reactant along the length of an isothermal, nonideal flow chemical reactor:

$$\frac{1}{Pe}\frac{d^2c}{dx^2} - \frac{dc}{dx} - Da\cdot Q(c) = 0 \ , \ 0\leq x\leq 1 \qquad \text{(III-1)}$$

with

$$c = 1 + \frac{1}{Pe}\frac{dc}{dx} \ , \quad \text{at} \quad x=0^+ \qquad \text{(III-2)}$$

$$\frac{dc}{dx} = 0, \quad \text{at} \quad x=1 \qquad \text{(III-3)}$$

where c = dimensionless measure of the composition of the reactant,

x = dimensionless measure of the distance from the reactor inlet,

Pe = Peclet number, vL/E,

Da = Damkohler number, $\frac{L}{v} k c_0^{n-1}$, for homogeneous reactors,

$Q(c)$ = term accounting for the kinetics of the decomposition, assumed to be of the form c^n,

v = superficial velocity,

n = reaction order,

L = tube length,

E = axial dispersion coefficient,

k = reaction rate constant,

c_0 = reactant composition at $x=0^+$.

The derivation of Equation (III-1) can be found in Levenspiel (21). The boundary conditions (III-2) and (III-3) have been discussed by Dankwerts (7), Wehner (29), and Pearson (24).

A discontinuity at the left endpoint, Equation (III-2), is the mathematical approximation of a given physical situation. It is for this reason that limits from the right must be considered near this end point.

In Equations (III-1) and (III-2) Pe accounts for the nonideality in flow; Pe $\to$ 0 corresponds to complete mixing in the tube, Pe $\to \infty$ corresponds to plug-flow behavior.

The aim of this chapter is to estimate Da, Pe, and n, given a set of observations $\{\tilde{c}_i, x_i;\ i=1,2,\ldots,N\}$, where $\tilde{c}_i$ stands for the observed value of composition at $x = x_i$.

B. Error Model

The solution of Equations (III-1) to (III-3) is:

$$c(x) = 1 - Da\left[\int_0^x Q(c(\xi))d\xi + \int_x^1 e^{Pe(x-\xi)} Q(c(\xi))d\xi\right] \qquad \text{(III-4)}$$

where ξ is a dummy variable introduced in order to carry out

the integrations.

Replacing Q(c) in Equation (III-4) by c^n gives:

$$c(x) = 1 - Da[\int_0^x c^n(\xi)d\xi + \int_x^1 e^{Pe(x-\xi)}c^n(\xi)d\xi] \qquad \text{(III-5)}$$

Let $c^n(x)$ be approximated by a polynomial of degree M:

$$c^n(x) \tilde{=} \sum_{m=0}^{M} a_m x^m \qquad \text{(III-6)}$$

Combining Equations (III-5) and (III-6), and replacing the left-hand side by $\tilde{c}_i$, the observed value of composition at $x = x_i$, gives the following error model in discretized form:

$$\varepsilon_i = c_i - 1 + Da[\int_0^{x_i} \sum_{m=0}^{M} a_m \xi^m d\xi + \int_{x_i}^1 e^{Pe(x_i-\xi)} \sum_{m=0}^{M} a_m \xi^m d\xi];$$

$$i=1,2,\ldots,N \qquad \text{(III-7)}$$

or

$$\varepsilon_i = c_i - 1 + \sum_{m=0}^{M} b_m [\int_0^{x_i} \xi^m d\xi + \int_{x_i}^1 \xi^m e^{Pe(x_i-\xi)} d\xi];$$

$$i=1,2,\ldots,N \qquad \text{(III-8)}$$

where

$$b_m = Da \cdot a_m; \quad m=0,1,\ldots,M \; . \qquad \text{(III-9)}$$

The analytical integration of the terms in Equation (III-8) is quite straightforward. With the error model given by Equation (III-8), the objective function to be minimized is:

$$S_1 = \sum_{i=1}^{N} w_i \varepsilon_i^2 \qquad \text{(III-10)}$$

where w_i; i=1,2,...,N are weights, introduced to reflect the precision of each individual observation.

Although the original purpose was the estimation of Da, Pe, and n, given a set of observations, the problem has now been transformed into one involving the estimation of Pe and b_m; m=0,1,...,M. In the related model described by Equation (III-8) Da and n do not appear explicitly; they have been lumped into the b_m's. This makes it necessary to use a two-phase estimation procedure consisting of:

Phase 1: The simultaneous estimation of:

(a) the effect of the nonlinearity in flow (accounted for by Pe), and

(b) the effect of the decomposition rate (accounted for by b_m; m=0,1,...,M) on the composition profile.

Phase 2: The subsequent estimation of Da and n.

Phase 1 involves minimization of the objective function S_1, given by Equation (III-9). This is accomplished by using the nonlinear least-squares technique. At the end of Phase 1, estimates of Pe and b_m; m=0,1,...,M are available; these will be denoted by $\hat{Pe}$ and $\hat{b}_m$; m=0,1,...,M.

From the inspection of Equations (III-6) and (III-9) it follows that:

$$Da \cdot c^n(x) \tilde{=} \sum_{m=0}^{M} b_m x^m \quad . \qquad \text{(III-11)}$$

The required error model for Phase 2 is obtained by combining Equations (III-8) and (III-11):

$$\varepsilon_i' = \sum_{m=0}^{M} \hat{b}_m x_i^m - Da\{1 - \sum_{m=0}^{M} \hat{b}_m [\int_0^{x_i} \xi^m d\xi + \int_{x_i}^{1} \xi^m e^{\hat{P}e(x_i - \xi)} d\xi]\}^n;$$

$$i = 1, 2, \ldots, N \qquad \text{(III-12)}$$

The objective function to be minimized is:

$$S_2 = \sum_{i=1}^{N} w_i (\varepsilon_i')^2 \qquad \text{(III-13)}$$

Note that the model given by Equation (III-12) is linear with respect to Da and n, when transformed into logarithmic coordinates. This procedure reduces the computation time required for Phase 2 considerably, compared to that for Phase 1. However, it is realized that the error distribution has also been transformed.

C. Generation of Data

1. Generation of Noise-Free Data

For n=1, the analytical solution of Equations (III-1) to (III-3) was used to generate the noise-free observations at eleven equally spaced points along the length of the reactor, corresponding to various Da and Pe values. The numerical solution for n=2 was taken from Creswell and Quon (6).

For n=1, the analytical solution is given by

$$c_i^* = k_1 \exp[Pe(1+\beta)x_i/2] + k_2 \exp[-Pe(\beta-1)x_i/2];$$

$$i=1,2,\ldots,11 \qquad \text{(III-14)}$$

where $$k_1 = \frac{2(\beta-1)}{(\beta+1)^2 \exp(\beta \cdot Pe) - (\beta-1)^2} \qquad \text{(III-15)}$$

$$k_2 = \frac{2(\beta+1)}{(\beta+1)^2 - (\beta-1)^2 \exp(-\beta \cdot Pe)} \qquad \text{(III-16)}$$

$$\beta = (1 + 4\,\frac{Da}{Pe})^{1/2} \qquad \text{(III-17)}$$

c_i^* = noise-free observation of c at $x = x_i$.

The various data sets used are coded in Table III-1. The noise-free observations corresponding to those data sets are shown in Tables III-2 to III-7.

TABLE III-1

CODING OF THE VARIOUS DATA SETS USED

Data Set	Da	Pe	n(known)	n(unknown)
A	1.500	6.000	1.000	--
B	3.000	6.000	1.000	--
C	1.500	50.00	1.000	--
D	3.000	50.00	1.000	--
E	2.000	6.000	--	1.000
F	2.000	6.000	--	2.000

TABLE III-2

NOISE-FREE OBSERVATIONS

DATA SET A

x	$c^*(x)$
0.0	0.82846
0.1	0.73168
0.2	0.64625
0.3	0.57088
0.4	0.50448
0.5	0.44616
0.6	0.39531
0.7	0.35179
0.8	0.31620
0.9	0.29062
1.0	0.28012

TABLE III-3

NOISE-FREE OBSERVATIONS

DATA SET B

x	$c^*(x)$
0.0	0.73205
0.1	0.58772
0.2	0.47186
0.3	0.37886
0.4	0.30427
0.5	0.24451
0.6	0.19683
0.7	0.15922
0.8	0.13056
0.9	0.11103
1.0	0.10324

TABLE III-4

NOISE-FREE OBSERVATIONS

DATA SET C

x	$c^*(x)$
0.0	0.97167
0.1	0.83989
0.2	0.72597
0.3	0.62751
0.4	0.54240
0.5	0.46884
0.6	0.40525
0.7	0.35029
0.8	0.30278
0.9	0.26175
1.0	0.23272

TABLE III-5

NOISE-FREE OBSERVATIONS

DATA SET D

x	$c^*(x)$
0.0	0.94627
0.1	0.71240
0.2	0.53634
0.3	0.40378
0.4	0.30399
0.5	0.22886
0.6	0.17230
0.7	0.12971
0.8	0.09765
0.9	0.07353
1.0	0.05832

TABLE III-6

NOISE-FREE OBSERVATIONS

DATA SET E

x	$c^*(x)$
0.0	0.79130
0.1	0.67550
0.2	0.57668
0.3	0.49237
0.4	0.42051
0.5	0.35942
0.6	0.30779
0.7	0.26483
0.8	0.23054
0.9	0.20633
1.0	0.19649

TABLE III-7

NOISE-FREE OBSERVATIONS

DATA SET F

x	$c^*(x)$
0.0	0.83129
0.1	0.74012
0.2	0.66559
0.3	0.60372
0.4	0.55172
0.5	0.50764
0.6	0.47017
0.7	0.43862
0.8	0.41305
0.9	0.39476
1.0	0.38727

2. Generation of Noisy Data

Each solution, c_i^*, corresponding to a certain Da, Pe, and n was contaminated with the addition of random numbers to generate twenty sets of noisy observations, using:

$$\tilde{c}_{ij} = c_i^* + \tilde{\varepsilon}_{ij} \; ; \quad i=1,2,\ldots,11; \quad j=1,2,\ldots,20 \qquad \text{(III-18)}$$

where c_i^* = true solution at $x = x_i$,

$\tilde{c}_{ij}$ = noisy observation at $x = x_i$, for the jth run,

$\tilde{\varepsilon}_{ij}$ = random number with Gaussian distribution, having zero mean and a standard deviation of 0.03, i.e., $f(\tilde{\varepsilon}) = f_N(\tilde{\varepsilon}|0, 0.0009)$.

Subroutines GAUSS and RANDU, supplied by the IBM 1130 scientific subroutine Package (13) were used for this purpose.

D. Treatment of Data

1. Weights and Initial Guesses of Parameters

All the computations were done using equal weights. This choice was based on the knowledge of the distribution of the observation errors, since they were all generated from the same parent distribution. The weighting matrix used was:

$$\underline{W}_{(NxN)} = \frac{1}{\sigma^2} \underline{I}_{(NxN)} \qquad \text{(III-19)}$$

where $I_{(NxN)}$ = the identity matrix,

σ^2 = variance estimate of the measurements.

For the minimization of S_1 σ was set equal to 0.03. For the minimization of S_2, σ^2 was approximated by

$$\frac{\sum_{i=1}^{N} \varepsilon_i'^2}{N - p} \qquad \text{(III-20)}$$

where p is the number of parameters estimated in Phase 2.

For the noise-free observations, second, third, and fourth degree approximating polynomials were tried. For the noisy observations, attempts to use polynomials with degrees higher than two resulted in parameter estimates with high variances. The initial guesses of Pe and b_m; m=0,1,...,M for the noise-free and noisy observations are shown in Tables III-8 and III-9.

2. Treatment of the Results Obtained from Noisy Measurements

It was noted before that for every set of Da, Pe, and n, twenty sets of noisy observations were generated; the results of the individual runs were averaged and statistical conclusions were drawn regarding the means and variances of the parameter estimates.

The nomenclature given below will be used throughout the remainder of this work:

$$\tilde{S}_p^2 = \frac{\sum_{j=1}^{J} (\hat{P}_j - \bar{P})^2}{J - 1} = \frac{\sum_{j=1}^{J} \hat{P}_j^2}{J - 1} - \frac{(\sum_{j=1}^{J} \hat{P}_j)^2}{J(J-1)} \qquad \text{(III-21)}$$

$$\bar{S}_p^2 = \frac{\sum_{j=1}^{J} \hat{S}_{p,j}^2}{J} \qquad \text{(III-22)}$$

$$\bar{p} = \frac{\sum_{j=1}^{J} \hat{P}_j}{J} \qquad \text{(III-23)}$$

$\hat{P}_j$ = least-squares estimate of parameter p, obtained from the jth run,

$\hat{S}_{p,j}^2$ = least-squares estimate of the variance of p, obtained from the jth run.

In words, $\tilde{S}_p^2$ is the variance of parameter p, obtained from the individual parameter estimates, whereas $\bar{S}_p^2$ is the variance of p, obtained by averaging the estimates of parameter variances predicted by individual least-squares runs. $\bar{p}$ is the mean of the individual estimates of p.

E. Results and Discussion

1. Noise-Free Observations

In Tables III-10 and III-11 results for Da, Pe, and n are shown for noise-free observations.

A study of these tables shows that the estimates of Da are closer to their true values for the case where n is considered known than for the case where it is treated as an unknown. (The estimate of Pe would not be affected by this choice, since its estimation is carried out in Phase 1.) Note also that, better estimates are obtained with increasing

TABLE III-8

INITIAL GUESSES OF THE PARAMETERS

NOISE-FREE OBSERVATIONS

Degree of Approximating Polynomial	$b_0^{(0)}$	$b_1^{(0)}$	$b_2^{(0)}$	$b_3^{(0)}$	$b_4^{(0)}$	$Pe^{(0)}$
2	5.0	-5.0	5.0	--	--	20.0
3	5.0	-5.0	10.0	-5.0	--	20.0
4	5.0	-5.0	5.0	-5.0	5.0	20.0

TABLE III-9

INITIAL GUESSES OF THE PARAMETERS

NOISY OBSERVATIONS

Data Set	$b_0^{(0)}$	$b_1^{(0)}$	$b_2^{(0)}$	$Pe^{(0)}$
A,B,E,F	5.0	-5.0	5.0	20.0
C,D	5.0	-5.0	5.0	100.0

TABLE III-10

PARAMETER ESTIMATES WITH n=1.0 (KNOWN)

NOISE-FREE OBSERVATIONS

Data Set	A		B		C		D	
Degree of Approximating Polynomial	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$
2	1.497	5.981	2.950	5.836	1.495	48.00	2.912	42.06
3	1.498	5.993	2.985	5.967	1.499	49.85	2.980	48.87
4	1.503	6.021	3.000	6.000	1.500	50.01	2.997	49.86

TABLE III-11

PARAMETER ESTIMATES WITH n UNKNOWN

NOISE-FREE OBSERVATIONS

Data Set	E			F		
Degree of Approximating Polynomial	$\hat{Da}$	$\hat{Pe}$	$\hat{n}$	$\hat{Da}$	$\hat{Pe}$	$\hat{n}$
2	1.981	5.946	0.990	1.870	5.759	1.881
3	2.000	5.980	1.002	1.981	5.934	1.990
4	2.004	6.003	1.003	1.992	5.990	1.994

polynomial degree. This, however, does not mean that the degree of the approximating polynomial can be increased indefinitely; the minimum variance criterion to be discussed later in this chapter would be the dictating factor in this choice.

2. Noisy Observations

The results of individual runs from one to twenty for different parameter sets are shown in Tables III-13 to III-18. All the results were obtained using second degree approximating polynomials. The summarized statistical results are given in Table III-12, in accordance with the nomenclature given in Section D.2 of this chapter.

Note that in Table III-12, some of the results for Pe have not been shown for Data Sets C and D. Studying Tables III-15 and III-16 shows that the variance estimates for Pe fluctuate widely. In Table III-15 the estimates of Pe also fluctuate widely. Thus, any statistical conclusions drawn from these results would not have much significance.

Studying Table III-12, the following conclusions are drawn for the range of investigation:

(a) The estimates of Pe are highly sensitive to the observation errors.

(b) The normalized standard deviation of the estimates of Da, $(\tilde{S}^2_{Da})^{1/2}/\bar{Da}$, is relatively insensitive to the value of Da, but inversely proportional to the value of Pe.

(c) The normalized standard deviation of the estimates

TABLE III-12

STATISTICAL RESULTS FROM NOISY OBSERVATIONS

Data Set	A	B	C	D	E	F
$\overline{Da}$	1.507	2.951	1.495	2.895	1.872	1.736
$\overline{n}$	--	--	--	--	0.903	1.684
$\overline{Pe}$	6.791	6.320	--	46.60	6.591	6.566
$\tilde{S}^2_{Da}$	0.0168	0.0572	0.0041	0.0148	0.1579	0.3066
$\tilde{S}^2_{n}$	--	--	--	--	0.0745	0.3957
$\tilde{S}^2_{Pe}$	4.847	1.790	--	218.0	3.118	4.844
$\overline{S}^2_{Da}$	0.0110	0.0217	0.0032	0.0107	0.0946	0.1920
$\overline{S}^2_{n}$	--	--	--	--	0.0229	0.1371
$\overline{S}^2_{Pe}$	7.290	2.593	--	--	4.889	7.534
$\frac{(\tilde{S}^2_{Da})^{1/2}}{\overline{Da}}$	0.086	0.081	0.043	0.042	0.212	0.319
$\frac{(\tilde{S}^2_{n})^{1/2}}{\overline{n}}$	--	--	--	--	0.302	0.373
$\frac{(\tilde{S}^2_{Pe})^{1/2}}{\overline{Pe}}$	0.212	0.313	--	0.317	0.286	0.335

TABLE III-13

INDIVIDUAL ESTIMATES

DATA SET A

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10$
1	6.967	1.424	10.823	0.062
2	4.271	1.224	7.801	0.552
3	8.129	1.684	8.347	0.054
4	4.411	1.444	4.174	0.027
5	7.198	1.620	4.459	0.031
6	4.258	1.396	4.327	0.086
7	5.369	1.329	7.973	0.119
8	6.703	1.515	6.046	0.160
9	6.584	1.593	5.109	0.186
10	6.841	1.471	7.546	0.025
11	5.322	1.414	6.954	0.108
12	4.345	1.366	4.551	0.165
13	7.964	1.621	6.750	0.200
14	5.706	1.553	5.497	0.035
15	5.040	1.404	5.562	0.024
16	9.882	1.626	14.706	0.005
17	6.403	1.597	5.430	0.054
18	12.659	1.701	18.511	0.196
19	7.655	1.528	8.457	0.028
20	10.106	1.674	12.454	0.080

TABLE III-14

INDIVIDUAL ESTIMATES

DATA SET B

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10$
1	6.396	2.745	3.568	0.160
2	4.810	2.433	2.929	0.884
3	7.098	3.223	3.011	0.044
4	4.761	2.951	1.950	0.100
5	6.606	3.084	2.846	0.174
6	4.692	2.777	2.007	0.108
7	5.457	2.595	2.978	0.220
8	6.353	2.924	2.511	0.422
9	6.338	3.133	2.268	0.452
10	6.379	2.926	2.875	0.051
11	5.410	2.750	2.729	0.259
12	4.746	2.677	2.074	0.237
13	7.188	3.210	2.687	0.435
14	5.681	3.008	2.360	0.139
15	5.229	2.787	2.370	0.041
16	8.124	3.087	4.239	0.036
17	6.108	3.149	2.324	0.105
18	9.753	3.313	4.804	0.323
19	6.928	3.008	3.096	0.045
20	8.343	3.247	3.855	0.109

TABLE III-15

INDIVIDUAL ESTIMATES

DATA SET C

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10^2$
1	6.212×10^3	1.454	6.02×10^{11}	0.45
2	135.51	1.459	1.86×10^5	0.72
3	119.40	1.614	5.34×10^4	0.27
4	18.28	1.438	1.17×10^2	0.35
5	83.71	1.578	1.75×10^4	0.25
6	23.15	1.421	2.50×10^2	0.23
7	101.50	1.409	5.80×10^4	0.36
8	49.28	1.441	2.63×10^3	0.51
9	27.68	1.477	3.21×10^2	0.33
10	90.01	1.472	2.31×10^4	0.10
11	45.90	1.460	2.90×10^3	0.50
12	32.53	1.412	7.35×10^2	0.48
13	51.39	1.525	2.32×10^3	0.51
14	33.08	1.514	7.23×10^2	0.20
15	45.13	1.460	2.08×10^3	0.02
16	124.12	1.550	8.67×10^4	0.04
17	45.88	1.557	1.62×10^3	0.31
18	180.61	1.596	2.50×10^5	0.56
19	94.53	1.480	2.88×10^4	0.04
20	85.20	1.579	1.63×10^4	0.12

TABLE III-16

INDIVIDUAL ESTIMATES

DATA SET D

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe} \times 10^{-3}$	$\hat{S}^2_{Da} \times 10$
1	82.29	2.781	6.598	0.087
2	58.24	2.733	2.016	0.185
3	61.84	3.103	1.632	0.087
4	24.03	2.918	0.082	0.116
5	55.75	2.966	1.277	0.174
6	28.06	2.798	0.138	0.054
7	56.63	2.709	1.744	0.072
8	43.17	2.779	0.533	0.155
9	32.66	2.911	0.191	0.100
10	54.45	2.892	1.186	0.036
11	44.49	2.814	0.707	0.118
12	32.85	2.725	0.232	0.118
13	45.13	2.996	0.528	0.140
14	35.27	2.912	0.279	0.103
15	39.75	2.843	0.419	0.034
16	124.60	2.958	26.235	0.076
17	39.80	3.023	0.353	0.105
18	138.47	3.094	31.714	0.174
19	57.79	2.893	1.487	0.029
20	97.61	3.060	9.085	0.088

TABLE III-17

INDIVIDUAL ESTIMATES

DATA SET E

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{n}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10$	$\hat{S}^2_{n} \times 10$
1	6.717	2.096	1.110	6.591	1.972	0.357
2	4.584	1.327	0.598	5.068	1.926	0.768
3	7.643	2.456	1.216	5.311	0.309	0.041
4	4.606	2.281	1.197	3.020	1.430	0.232
5	6.944	1.679	0.687	4.893	0.297	0.074
6	4.498	1.397	0.569	3.121	0.017	0.007
7	5.454	1.600	0.787	5.173	0.601	0.191
8	6.575	1.385	0.572	4.142	0.993	0.451
9	6.510	1.619	0.761	3.617	1.879	0.622
10	6.651	2.424	1.329	4.947	0.119	0.019
11	5.407	1.707	0.797	4.624	0.602	0.153
12	4.659	1.191	0.383	3.255	0.088	0.052
13	7.631	2.021	1.067	4.528	3.127	0.694
14	5.731	1.617	0.665	3.824	0.124	0.034
15	5.167	1.726	0.852	3.851	0.059	0.017
16	9.028	2.089	0.981	8.362	0.064	0.011
17	6.293	1.953	0.948	3.768	0.819	0.178
18	11.205	2.381	1.241	9.964	3.241	0.484
91	7.341	2.209	1.166	5.441	0.206	0.037
20	9.259	2.292	1.135	7.348	1.042	0.158

TABLE III-18

INDIVIDUAL ESTIMATES

DATA SET F

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{n}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da}$x10	$\hat{S}^2_{n}$x10
1	6.715	1.918	2.065	10.958	3.383	1.904
2	3.999	0.813	0.683	7.935	1.655	4.702
3	7.904	2.579	2.411	8.390	1.316	0.404
4	4.224	2.365	2.361	4.210	2.953	1.128
5	6.970	1.504	1.296	7.483	0.492	0.406
6	4.050	1.109	0.925	4.356	0.065	0.114
7	5.105	1.269	1.294	8.056	0.645	0.855
8	6.491	1.148	1.039	6.051	1.538	2.666
9	6.389	1.471	1.500	5.114	3.771	3.904
10	6.615	2.492	2.599	7.598	0.429	0.161
11	5.105	1.423	1.373	7.027	0.695	0.669
12	4.118	0.882	0.525	4.572	0.159	0.450
13	7.765	2.033	2.171	6.767	7.897	4.412
14	5.497	1.413	1.220	5.524	0.248	0.238
15	4.804	1.497	1.527	5.600	0.043	0.043
16	9.637	1.966	1.857	14.837	0.156	0.077
17	6.195	1.921	1.887	5.446	2.066	1.188
18	12.430	2.436	2.460	18.667	7.769	2.835
19	7.435	2.183	2.261	8.510	0.673	0.319
20	9.877	2.308	2.228	12.530	2.458	0.947

of Pe, $(\tilde{S}^2_{Pe})^{1/2}/\bar{Pe}$, is directly proportional to the value of Pe, and inversely proportional to the value of Da.

(d) The normalized standard deviation of all three parameter estimates are directly proportional to the value of n.

(e) $(\tilde{S}^2_{Da})^{1/2}/\bar{Da}$ is higher for the case where n is unknown than for the case where n is known.

The last observation suggests that the estimate of the effect of the combined reaction parameters (i.e., Da·Q(c)) would be more reliable than the individual estimate of Da and n themselves. This limitation is not surprising when one keeps in mind the set up of the estimation procedure in which a polynomial is introduced to approximate the *combined* effect of Da and n.

Note also that the estimate of Pe does not depend on one's knowledge about n; regardless of whether n is known or unknown the same estimate of Pe will be obtained in both cases. This fact is also due to the way the estimation procedure has been set up, which consists of two phases. It also makes sense physically; it cannot be expected that the knowledge about a kinetic term (i.e., n) should affect a dispersion characteristic term (i.e., Pe), whereas it is natural for it to affect another kinetic term, i.e., Da.

F. Comments on the Error Model

(a) Note that the right-hand side of Equation (III-12) is a continuous function of x. This suggests that the evalua-

tion of the model error is not restricted to the use of the original x values at which data was taken. Thus, the number of points used in Phase 2 could be increased indefinitely. In the limit, the objective function S_2 would be expressed as an integral of the model error over the interval (0,1). Equations (III-12) and (III-13) in continuous form become:

$$\varepsilon(x) = \sum_{m=0}^{M} \hat{b}_m x^m - Da\{1 - \sum_{m=0}^{M} \hat{b}_m [\int_0^x \xi^m d\xi + \int_x^1 \xi^m e^{\hat{Pe}(x-\xi)} d\xi]\}^n; \quad \text{(III-24)}$$

$$S = \int_0^1 w(x)\varepsilon^2(x)dx \quad \text{(III-25)}$$

The use of the above model is restricted to the case where n is a known integer; in this case, a quadratic expression in terms of Da (as the only unknown) would be obtained. The choice of the reasonable root would be subject to inspection. Note that the algebra involved would get more and more complicated with increasing n.

Equations (III-24) and (III-25) could be used to express Da as an analytical function of Pe and b_m; m=0,1,...,M.

$$Da = F(Pe,\underline{b}) \quad \text{(III-26)}$$

The estimates of the expected values, variances, and covari-

ances of Pe and b_m; m=0,1,...,M would readily be available from Phase 1. The following relationships would give an estimate of the expected value and variance of Da:

$$E(Da) \cong F(\hat{Pe},\underline{\hat{b}}) + \frac{1}{2}\sum_{m=0}^{M}\frac{\partial^2 F}{\partial b_m^2}\hat{S}^2_{b_m} + \frac{1}{2}\frac{\partial^2 F}{\partial Pe^2}\hat{S}^2_{Pe} \qquad \text{(III-27)}$$

$$V(Da) \cong \sum_{m=0}^{M}\left(\frac{\partial F}{\partial b_m}\right)^2 \hat{S}^2_{b_m} + \left(\frac{\partial F}{\partial Pe}\right)^2 \hat{S}^2_{Pe}$$

$$+ 2\left(\frac{\partial F}{\partial b_0}\right)\left(\frac{\partial F}{\partial b_1}\right)cov(b_0,b_1)$$

$$+ 2\left(\frac{\partial F}{\partial b_M}\right)\left(\frac{\partial F}{\partial Pe}\right)cov(b_M,Pe) \qquad \text{(III-28)}$$

where $E(Da)$ = expected value of Da,

$V(Da)$ = variance of Da,

$\hat{S}^2_{Pe}$ = variance of Pe,

$\hat{S}^2_{b_m}$ = variance of b_m,

$cov(b_j,Pe)$ = covariance of b_j and Pe,

$cov(b_j,b_k)$ = covariance of b_j and b_k; $j \neq k$.

All the terms on the right-hand sides of Equations (III-27) and (III-28) should be evaluated at the expected values of Pe and $\underline{b}$, that is, $\hat{Pe}$ and $\underline{\hat{b}}$. The second and third terms on the right-hand side of Equation (III-27) could preferentially

be omitted without any serious loss of accuracy. Thus, only the calculation of the first derivatives would be necessary.

(b) One could also consider solving the following equation for Da:

$$\int_0^1 w(x)\varepsilon(x)dx = 0 \qquad \text{(III-29)}$$

Although the computations involved in solving Equation (III-29) for Da would be much simpler compared to the computations involved in solving Equation (III-25), it should be kept in mind that the former sets the integral of the weighted model errors equal to zero, whereas the latter minimizes the integral of the weighted squares of the model errors, undoubtedly, a sounder criterion.

G. Comparison with a New Model

In order to test the effectiveness of the method, the results were compared with those obtained by estimating the coefficients of the approximating polynomial prior to the estimation of the parameters of interest, using the same old data.

1. Error Model

For convenience, Equation (III-5) is reproduced below:

$$c(x) = 1 - Da\left[\int_0^x c^n(\xi)d\xi + \int_x^1 e^{Pe(x-\xi)}c^n(\xi)d\xi\right] \qquad \text{(III-30)}$$

Suppose this time $c(x)$, instead of $c^n(x)$, is approximated by a polynomial of degree K:

$$c(x) \tilde{=} \sum_{m=0}^{K} \hat{a}_m x^m \qquad \text{(III-31)}$$

Combining Equations (III-30) and (III-31), and replacing the left-hand side by $\tilde{c}_i$, the observed value of composition at $x = x_i$, gives the following error model in discretized form:[1]

$$\varepsilon_i = \tilde{c}_i - 1 + Da\left[\int_0^{x_i} \left(\sum_{m=0}^{K} \hat{a}_m \xi^m\right)^n d\xi + \int_{x_i}^{1} e^{Pe(x_i-\xi)} \left(\sum_{m=0}^{K} \hat{a}_m \xi^m\right)^n d\xi\right];$$

$$i=1,2,\ldots,N \qquad \text{(III-32)}$$

Suppose that the coefficients of the approximating polynomial have been estimated beforehand; call these estimates $\hat{a}_m$; $m=0,1,\ldots,K$. Note that K now represents the optimum polynomial degree, the estimation of which will be described in the next section. Replacing the unknown coefficients in

---

[1] ε_i has been used in denoting both model errors defined by Equations (III-8) and (III-32), although they are different; this has been done for notational simplicity. Throughout the remainder of this work, the ε's and S's should be interpreted only in the context of the model by which they are defined.

Equation (III-32) by their estimates, the error model becomes:

$$\varepsilon_i' = \tilde{c}_i - 1 + Da\left[\int_0^{x_i} \left(\sum_{m=0}^{K} \hat{a}_m \xi^m\right)^n d\xi + \int_{x_i}^{1} e^{Pe(x_i-\xi)} \left(\sum_{m=0}^{K} \hat{a}_m \xi^m\right)^n d\xi\right];$$

$$i=1,2,\ldots,N \qquad \text{(III-33)}$$

The above model can be used to estimate Da and Pe simultaneously provided n is a known integer, since, otherwise the analytical integration of the terms in Equation (III-33) is not possible. Those terms will progressively get more complicated with increasing n. Note also that $\tilde{c}_i$ could have been replaced by its approximating polynomial.

The above model was tested for n = 1. In this case, Equation (III-33) simplifies to:

$$\varepsilon_i' = \tilde{c}_i - 1 + Da \sum_{m=0}^{K} \hat{a}_m\left[\int_0^{x_i} \xi^m d\xi + \int_{x_i}^{1} \xi^m e^{Pe(x_i-\xi)} d\xi\right];$$

$$i=1,2,\ldots,N \qquad \text{(III-34)}$$

Again, unit weights were used in the minimization of:

$$S = \sum_{i=1}^{N} w_i (\varepsilon_i')^2 \qquad \text{(III-35)}$$

2. Treatment of Data

Forsythe's method (10) was used in generating polynomials in x to approximate the composition measurements.[1] The best-fit polynomial for the jth data set was chosen after observing the variance $S^2_{k,j}$ for different k values, ranging from two to five:

$$S^2_{k,j} = \frac{\sum_{i=1}^{N} (\hat{c}_{k,ij} - \tilde{c}_{ij})^2}{N - (k+1)} \qquad \text{(III-36)}$$

where $\tilde{c}_{ij}$ = observation at $x = x_i$, for the jth run,

---

[1] Note that the method itself is based on the approximation of a set of measurements by:

$$\sum_{m=0}^{k} \hat{\alpha}_m \phi_m(x) \qquad \text{(i)}$$

where $\phi_m(x)$; m=0,1,...,k are functions of x. Using the appropriate relationships, the above expression can be transformed to a polynomial in x:

$$\sum_{m=0}^{k} \hat{a}_m x^m \; . \qquad \text{(ii)}$$

The motivation behind using Forsythe's method stems from the fact that ill-conditioning encountered with high polynomial degrees can be avoided due to the orthogonality of $\phi_m(x)$; m=0,1,...,k. Once they and their coefficients have been calculated, the transformation to (ii) is trivial.

$\hat{c}_{k,ij}$ = corresponding value obtained by evaluating the jth approximating polynomial of degree k at $x = x_i$.

A flexible variance criterion was defined; for the jth run, the polynomial with minimum variance $S^2_{k,j}$ was chosen to represent the data. In cases where $S^2_{k,j}$ kept decreasing slowly with increasing k, that value of k for which the next higher order polynomial caused less than about 10% reduction in $S^2_{k,j}$ was picked.

The weighting matrix used is again given by Equation (III-19) with $\sigma = 0.03$.

3. Results and Discussion

(a) Noise-Free Observations

The results for noise-free observations are given in Table III-19. Again, note the improvement in the accuracy of the estimates with increasing polynomial degree.

(b) Noisy Observations

With data sets C and D, the original model seems to be superior as far as the estimates of Pe are concerned. The dependence of the estimates of Pe on the coefficients of the approximating polynomial cannot be overlooked, as was shown by a few runs with the same data set, but polynomials of different degrees. The results for Da, on the other hand, were quite good; even for ill-conditioned cases where $\hat{Pe}$ jumped to a value in the order 10^{12}, the corresponding $\hat{Da}$

TABLE III-19

PARAMETER ESTIMATES USING THE COMPARISON MODEL

NOISE-FREE OBSERVATIONS

Data Set	A		B		C		D	
Degree of Approximating Polynomial	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$	$\hat{Da}$	$\hat{Pe}$
2	1.499	6.000	2.992	6.107	1.498	50.98	2.969	52.09
3	1.499	6.005	2.997	6.011	1.499	50.06	2.995	50.80
4	1.500	5.999	3.000	5.999	1.500	49.86	2.999	50.09
5	1.500	6.001	3.000	6.000	1.500	49.96	3.000	50.00

was fairly close to the true value. This suggests that in cases where an accurate estimate of Pe is not available, the assumption of plug-flow behavior in the system will still give a fairly reliable estimate of Da.

The summarized statistical results for data sets A and B are shown in Table III-20. The individual results are shown in Tables III-21 and III-22.

H. Time Requirements

All the calculations for this and the next two problems were done using the IBM 1800 computer, with double precision. The time needed for computation was calculated by taking the difference between the time when computation ended and execution started. This included the time for building the coreload, reading the data, and printing. These, however, did not have an appreciable effect on the computing time, compared to the length of time spent on estimation.

(a) Approximating polynomial with unknown coefficients: average time required : 4 seconds/iteration

average number of iterations: 6-7 (per run)

(b) Approximating polynomial with known coefficients: As mentioned earlier, coefficients of the approximating polynomials were estimated prior to the estimation of the parameters of interest. For this purpose, a program was used which calculated the coefficients and their variances, for second, third, fourth, and fifth degree polynomials

TABLE III-20

STATISTICAL RESULTS FOR NOISY OBSERVATIONS

COMPARISON MODEL

Data Set	A	B
$\overline{Da}$	1.509	3.004
$\overline{Pe}$	6.705	6.578
$\tilde{s}^2_{Da}$	0.0036	0.0154
$\tilde{s}^2_{Pe}$	2.082	1.813
$\overline{s}^2_{Da}$	0.0010	0.0021
$\overline{s}^2_{Pe}$	1.123	0.651
$\frac{(\tilde{s}^2_{Da})^{1/2}}{\overline{Da}}$	0.040	0.041
$\frac{(\tilde{s}^2_{Pe})^{1/2}}{\overline{Pe}}$	0.215	0.205

TABLE III-21

INDIVIDUAL ESTIMATES USING THE COMPARISON MODEL

DATA SET A

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10^3$
1	8.437	1.532	1.9996	1.026
2	10.242	1.594	3.5335	1.041
3	5.786	1.542	0.6329	1.038
4	4.629	1.510	0.3379	1.005
5	7.807	1.605	1.4700	1.054
6	5.980	1.483	0.6925	0.977
7	8.373	1.493	1.9734	0.994
8	6.640	1.423	0.9750	0.939
9	5.292	1.455	0.4882	0.957
10	5.529	1.431	0.5856	0.966
11	7.772	1.574	1.4949	1.047
12	6.790	1.452	1.0182	0.951
13	4.982	1.431	0.4290	0.958
14	6.856	1.586	0.9845	1.039
15	6.111	1.471	0.7518	0.978
16	8.668	1.600	2.1013	1.070
17	5.317	1.500	0.4933	0.995
18	6.191	1.500	0.7949	1.025
19	6.029	1.457	0.7425	0.983
20	6.674	1.543	0.9630	1.038

TABLE III-22

INDIVIDUAL ESTIMATES USING THE COMPARISON MODEL

DATA SET B

Run No.	$\hat{Pe}$	$\hat{Da}$	$\hat{S}^2_{Pe}$	$\hat{S}^2_{Da} \times 10^3$
1	8.288	3.006	1.1352	2.026
2	9.591	3.112	1.6275	2.013
3	6.069	3.119	0.4909	2.268
4	4.857	3.092	0.2679	2.256
5	7.767	3.190	0.8915	2.156
6	5.848	2.943	0.4256	2.016
7	7.780	2.916	0.9480	1.948
8	5.953	2.787	0.4569	1.896
9	5.078	2.913	0.2936	2.041
10	5.439	2.860	0.3782	2.062
11	7.869	3.115	0.9396	2.095
12	6.218	2.836	0.4974	1.884
13	4.834	2.884	0.2697	2.082
14	6.886	3.171	0.6323	2.160
15	6.025	2.917	0.4696	2.011
16	8.722	3.172	1.2771	2.153
17	5.357	3.021	0.3455	2.164
18	6.239	3.021	0.5365	2.198
19	5.937	2.904	0.4712	2.071
20	6.800	3.097	0.6661	2.215

simultaneously. Time spent was about 8 seconds per run.

For the estimation of Da and Pe:

average time required : 4 seconds/iteration

average number of iterations: 8 (per run).

I. Others' Approaches

Lee (19) has attacked the same problem, with n=2 (known), using a different approach; in this case Equation (III-1) is reduced to two first order ordinary differential equations. Da and Pe are also treated as variables in x whose derivatives are equal to zero. The quasilinearization technique is applied to the resulting system of four ordinary differential equations; this technique requires the simultaneous integration of four homogeneous differential equations with four different initial condition sets, to generate four homogeneous solutions. Also a particular solution is generated by the integration of the system of four non-homogeneous differential equations. The initial conditions for the homogeneous and particular solutions are chosen such that two of the four unknown constants appearing in the expression for the general solution vector coincide with Da and Pe. The other two can be expressed in terms of Da and Pe. Least-squares procedure is carried out to find the values of Da and Pe which minimize a particular objective function which is non-linear in Pe. To this end, a random search technique has been used. Note that in Lee's approach non-linearity with respect to c(x) is dealt with by the use of quasilinea-

rization. Non-linearity with respect to the parameters (i.e., Pe) is taken care of by the use of a random search technique. In the present work, however, the only non-linearity to be considered is the non-linearity with respect to the parameters. Note, also, that the cumbersome integrations have been avoided by the use of a polynomial.

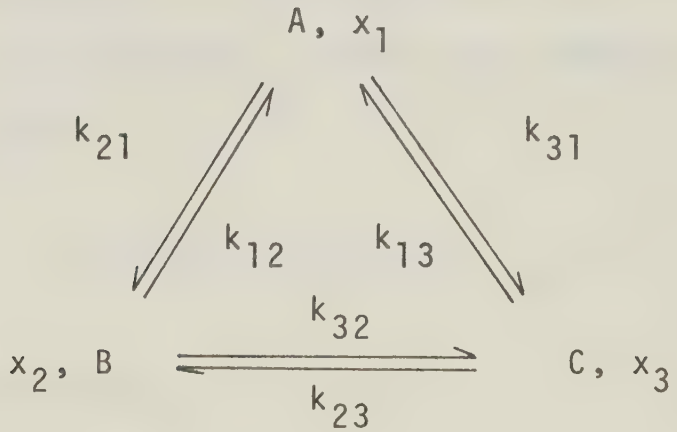
Cresswell and Quon's approach (6) has been to fit an orthogonal Forsythe polynomial to the composition measurements, and obtain analytical expressions for Da and Pe in terms of the coefficients of the polynomial using moment relations. It should be noted that the availability of the analytical expressions is restricted to the case where n is a known integer. In this case, numerical experimentation is possible by using a random number generating routine into which the estimates of the means and variances of the coefficients of the Forsythe polynomials are fed; using the analytical expressions for Da and n, estimates of their means and variances are obtained. For n being a non-integer, analytical expressions for Da and n are not available. Thus, the procedure described above for statistical analysis cannot be used in this case.

CHAPTER IV

A THREE-COMPONENT MONOMOLECULAR REVERSIBLE REACTION SYSTEM

A. Statement of the Problem

Consider the monomolecular reversible reaction system represented by:



x_1, x_2, and x_3 are dimensionless measures of the compositions of reactants A, B, and C, respectively. k_{ij}; i,j= 1,2,3, $i \neq j$, are the individual reaction rate constants. The differential equations describing the system are:

$$x_1' = -(k_{21} + k_{31})x_1 + k_{12}x_2 + k_{13}x_3 \qquad \text{(IV-1)}$$

$$x_2' = k_{21}x_1 - (k_{12} + k_{32})x_2 + k_{23}x_3 \qquad \text{(IV-2)}$$

$$x_3' = k_{31}x_1 + k_{32}x_2 - (k_{13} + k_{23})x_3 \qquad \text{(IV-3)}$$

subject to the initial conditions:

$$x_1(0) = x_{1,0} \ , \tag{IV-4}$$

$$x_2(0) = x_{2,0} \ , \tag{IV-5}$$

$$x_3(0) = x_{3,0} \ . \tag{IV-6}$$

In the notation above, prime denotes the time derivative of the variable in question. Since the compositions have been normalized, i.e.,

$$x_1 + x_2 + x_3 = 1; \quad t \geq 0 \tag{IV-7}$$

then it follows that:

$$x_1' + x_2' + x_3' = 0; \quad t \geq 0 \tag{IV-8}$$

Thus any two of the Equations (IV-1) to (IV-3) are sufficient to represent the system. Eliminating x_2 in Equation (IV-1) and (IV-3) using Equation (IV-7) gives:

$$x_1' = -(k_{21} + k_{12} + k_{31})x_1 + (k_{13} - k_{12})x_3 + k_{12} \tag{IV-9}$$

$$x_3' = (k_{31} - k_{32})x_1 - (k_{13} + k_{23} + k_{32})x_3 + k_{32} \tag{IV-10}$$

Let

$$\frac{k_{21}}{k_{12}} = K_1; \quad \frac{k_{32}}{k_{23}} = K_2; \quad \frac{k_{13}}{k_{31}} = K_3 \ , \tag{IV-11}$$

and for simplicity:

$$k_{12} = k_1; \quad k_{23} = k_2; \quad k_{31} = k_3 . \tag{IV-12}$$

K_1, K_2, and K_3 are equilibrium constants, whose values are assumed to be known for the purposes of this problem. With the help of Equations (IV-11) and (IV-12), Equations (IV-9) and (IV-10) take the following form:

$$x_1' = -[(1+K_1)k_1 + k_3]x_1 + (K_3k_3 - k_1)x_3 + k_1 \tag{IV-13}$$

$$x_3' = (k_3 - K_2k_2)x_1 - [(K_3k_3 + (1+K_2)k_2]x_3 + K_2k_2 \tag{IV-14}$$

subject to the initial conditions:

$$x_1(0) = x_{1,0} , \tag{IV-15}$$

$$x_3(0) = x_{3,0} . \tag{IV-16}$$

The aim in this chapter is to estimate k_1, k_2, and k_3, given the measurements of x_1 and x_3 at different values of t, starting from t=0.

B. Possible Error Models

The solution of Equations (IV-13) and (IV-14) in discretized form is:

$$x_{1,i} = x_{1,0}e^{-a_1 t_i} + \int_0^{t_i} e^{a_1(\xi - t_i)}[k_1 + b_1 x_3(\xi)]d\xi; \quad \text{(IV-17)}$$

$$x_{3,i} = x_{3,0}e^{-a_3 t_i} + \int_0^{t_i} e^{a_3(\xi - t_i)}[K_2 k_2 + b_3 x_1(\xi)]d\xi; \quad \text{(IV-18)}$$

$$i=1,2,\ldots,N$$

where $x_{1,i}$ and $x_{3,i}$ are the dimensionless measures of the compositions of the reactants A and C, respectively, at $t = t_i$. The remaining terms are defined below:

$$\begin{aligned} a_1 &= (1+K_1)k_1 + k_3 \\ a_3 &= K_3 k_3 + (1+K_2)k_2 \\ b_1 &= K_3 k_3 - k_1 \\ b_3 &= k_3 - K_2 k_2 \end{aligned} \quad \text{(IV-19)}$$

Note that although the original set of differential Equations (IV-13) and (IV-14) are linear with respect to the parameters, this is no longer the case for the solutions given by Equations (IV-17) and (IV-18).

One way to attack the problem would be to approximate x_1 and x_3 by polynomials in t, the coefficients of which are to be estimated simultaneously, with the original parameters of interest. To this end, let

$$x_1(t) = P(t) \tilde{=} \sum_{m=0}^{L} p_m t^m \qquad \text{(IV-20)}$$

$$x_3(t) = Q(t) \tilde{=} \sum_{m=0}^{L} q_m t^m \qquad \text{(IV-21)}$$

Combining Equations (IV-17) and (IV-18) with Equations (IV-20) and (IV-21) gives:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0}e^{-a_1 t_i} - \int_0^{t_i} e^{a_1(\xi - t_i)}[k_1 + b_1 \sum_{m=0}^{M} q_m \xi^m]d\xi; \qquad \text{(IV-22)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0}e^{-a_1 t_i} - \int_0^{t_i} e^{a_3(\xi - t_i)}[K_2 k_2 + b_3 \sum_{m=0}^{L} p_m \xi^m]d\xi; \qquad \text{(IV-23)}$$

$$i = 1,2,\ldots,N$$

where $\varepsilon_{1,i}, \varepsilon_{3,i}$ = model errors at $t = t_i$,

$\tilde{x}_{1,i}, \tilde{x}_{3,i}$ = observed values of x_1 and x_3 at $t = t_i$.

Rearranging the integrands in Equations (IV-22) and (IV-23) gives:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0}e^{-a_1 t_i} - k_1 \int_0^{t_i} e^{a_1(\xi - t_i)} d\xi$$

$$- b_1 \sum_{m=0}^{M} q_m \int_0^{t_i} \xi^m e^{a_1(\xi - t_i)} d\xi; \qquad \text{(IV-24)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0}e^{-a_3 t_i} - K_2 k_2 \int_0^{t_i} e^{a_3(\xi - t_i)} d\xi$$

$$- b_3 \sum_{m=0}^{L} p_m \int_0^{t_i} \xi^m e^{a_3(\xi - t_i)} d\xi; \quad i=1,2,\ldots,N \qquad \text{(IV-25)}$$

The integration of the above expressions is quite straightforward. The objective function to be minimized is:

$$S = \sum_{i=1}^{N} \left(\frac{1}{\sigma_1^2} \varepsilon_{1,i}^2 + \frac{1}{\sigma_3^2} \varepsilon_{3,i}^2 \right) \qquad \text{(IV-26)}$$

where σ_1^2 and σ_3^2 are estimates of the variances of the x_1 and x_3 measurements.

Attempts to minimize (IV-26) for the simultaneous estimation of k_1, k_2, k_3 and p_m, q_n; $m=0,1,\ldots,L$; $n=0,1,\ldots,M$ using the models defined by Equations (IV-24) and (IV-25) would prove unsuccessful, due to the interaction between various parameters. In the following section, some approaches which will circumvent this situation are described.

1. Nonlinear Polynomial Model I

Suppose the observations $\tilde{x}_{1,i}$ and $\tilde{x}_{3,i}$; i=1,2,...,N are approximated by polynomials in t, so that:

$$x_1(t) \cong \sum_{m=0}^{L} \hat{p}_m t^m \qquad \text{(IV-27)}$$

$$x_3(t) \cong \sum_{m=0}^{M} \hat{q}_m t^m \qquad \text{(IV-28)}$$

Comparing Equations (IV-20), (IV-21) and (IV-27), (IV-28), note that in the former L and M represent arbitrary polynomial degrees, whereas in the latter, they represent the optimum degrees chosen according to the minimum variance criterion described in Section G.2 of Chapter III. Note also that $\hat{p}_m$ and $\hat{q}_n$; m=0,1,...,L; n=0,1,...,M are the least-squares estimates of p_m and q_n.

Combining Equations (IV-17) and (IV-18) with Equations (IV-27) and (IV-28) gives:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0}e^{-a_1 t_i} - k_1 \int_0^{t_i} e^{a_1(\xi - t_i)}\, d\xi$$

$$- b_1 \sum_{m=0}^{M} \hat{q}_m \int_0^{t_i} \xi^m e^{a_1(\xi - t_i)}\, d\xi; \qquad \text{(IV-29)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0}e^{-a_3 t_i} - K_2 k_2 \int_0^{t_i} e^{a_3(\xi - t_i)}\, d\xi$$

$$- b_3 \sum_{m=0}^{L} \hat{p}_m \int_0^{t_i} \xi^m e^{a_3(\xi - t_i)}\, d\xi; \quad i=1,2,...,N \qquad \text{(IV-30)}$$

The model defined by Equations (IV-29) and (IV-30) will be called "Nonlinear Polynomial Model I" due to its nonlinearity with respect to parameters k_1, k_2, and k_3.

2. Linear Polynomial Model

Introducing Equations (IV-27) and (IV-28) into Equations (IV-13) and (IV-14) gives the following discretized model after integration:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - k_1 t_i + a_1 \sum_{m=0}^{L} \hat{p}_m \int_0^{t_i} \xi^m d\xi - b_1 \sum_{m=0}^{M} \hat{q}_m \int_0^{t_i} \xi^m d\xi; \qquad \text{(IV-31)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0} - K_2 k_2 t_i - b_3 \sum_{m=0}^{L} \hat{p}_m \int_0^{t_i} \xi^m d\xi + a_3 \sum_{m=0}^{M} \hat{q}_m \int_0^{t_i} \xi^m d\xi; \quad i=1,2,\ldots,N \qquad \text{(IV-32)}$$

or

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - k_1 t_i + a_1 \sum_{m=0}^{L} \frac{\hat{p}_m}{m+1} t_i^{m+1} - b_1 \sum_{m=0}^{M} \frac{\hat{q}_m}{m+1} t_i^{m+1}; \qquad \text{(IV-33)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0} - K_2 k_2 t_i - b_3 \sum_{m=0}^{L} \frac{\hat{p}_m}{m+1} t_i^{m+1}$$

$$+ a_3 \sum_{m=0}^{M} \frac{\hat{q}_m}{m+1} t_i^{m+1} \quad ; \quad i=1,2,\ldots,N \qquad \text{(IV-34)}$$

This model will be called "Linear Polynomial Model" due to its linearity with respect to the parameters of interest.

3. Nonlinear Exponential Model I

So far only polynomials have been considered as candidates for approximating the measurements of x_1 and x_3. Inspection of the composition profiles could suggest that the measurements be approximated by exponential functions:

$$x_1(t) \tilde{=} R(t) = r_0 + r_1 e^{-v_1 t} \qquad \text{(IV-35)}$$

$$x_3(t) \tilde{=} S(t) = s_0 + s_1 e^{-v_3 t} \qquad \text{(IV-36)}$$

If it is required that those functions should satisfy the initial and equilibrium values exactly, r_0, r_1, s_0, and s_1 should be chosen so that:

$$r_0 = x_{1,e}$$

$$r_1 = x_{1,0} - x_{1,e} \qquad \text{(IV-37)}$$

$$s_0 = x_{3,e}$$

$$s_1 = x_{3,0} - x_{3,e} \qquad \text{(IV-38)}$$

where $x_{1,e}$ and $x_{3,e}$ are the equilibrium compositions of reactants A and C respectively. With this choice Equations (IV-35) and (IV-36) become:

$$x_1(t) \tilde{=} x_{1,e} + (x_{1,0} - x_{1,e})e^{-v_1 t} \qquad \text{(IV-39)}$$

$$x_3(t) \tilde{=} x_{3,e} + (x_{3,0} - x_{3,e})e^{-v_3 t} \qquad \text{(IV-40)}$$

Combining Equation (IV-17) with Equation (IV-40) yields:

$$x_{1,i} = x_{1,0}e^{-a_1 t_i} + \int_0^{t_i} e^{a_1(\xi - t_i)}[k_1 + b_1 x_{3,e} + b_1(x_{3,0} - x_{3,e})e^{-v_3 \xi}]d\xi;$$

$$i=1,2,\ldots,N \qquad \text{(IV-41)}$$

Keeping in mind that:

$$k_1 + b_1 x_{3,e} - a_1 x_{1,e} = 0 \ , \qquad \text{(IV-42)}$$

since the left-hand side of Equation (IV-42) is equal to the rate of change of x_1 at equilibrium, Equation (IV-42)

reduces to:

$$x_{1,i} = x_{1,0}e^{-a_1 t_i} - a_1 x_{1,e} \int_0^{t_i} e^{a_1(\xi - t_i)} d\xi$$

$$+ b_1(x_{3,0} - x_{3,e}) \int_0^{t_i} e^{a_1(\xi - t_i)} e^{-v_3 \xi} d\xi \qquad \text{(IV-43)}$$

After performing the necessary integrations and rearranging, the following error model is obtained:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,e} - (x_{1,0} - x_{1,e})e^{-a_1 t_i}$$

$$+ b_1(x_{3,0} - x_{3,e}) \frac{e^{-a_1 t_i} - e^{-v_3 t_i}}{a_1 - v_3} \qquad \text{(IV-44)}$$

In the same manner,

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,e} - (x_{3,0} - x_{3,e})e^{-a_3 t_i}$$

$$+ b_3(x_{1,0} - x_{1,e}) \frac{e^{-a_3 t_i} - e^{-v_1 t_i}}{a_3 - v_1} \qquad \text{(IV-45)}$$

$$i=1,2,\ldots,N$$

This model will be called "Nonlinear Exponential

Model I". The least-squares objective function should be minimized to estimate k_1, k_2, k_3, v_1, and v_3 simultaneously.

The original choice of x_1 and x_3 to be approximated by exponential functions followed the inspection of the composition profile generated with certain initial conditions and k values which will be given later. With other numerical values, the resulting composition profiles could dictate that other reactant sets be approximated by exponential functions. In any case, it should be kept in mind that this approach is strictly dependent on the experimental observations.

4. Linear Exponential Model

Combining Equations (IV-39) and (IV-49) with Equation (III-13) gives, after integration:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - (k_1 + b_1 x_{3,e} - a_1 x_{1,e}) t_i$$

$$- a_1 (x_{1,0} - x_{1,e}) \frac{e^{-v_1 t_i} - 1}{v_1} - b_1 (x_{3,e} - x_{3,0}) \frac{e^{-v_3 t_i} - 1}{v_3};$$

$$i=1,2,\ldots,N \qquad \text{(IV-46)}$$

Noting again that:

$$k_1 + b_1 x_{3,e} - a_1 x_{1,e} = 0 \ ,$$

Equation (IV-46) reduces to:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - a_1(x_{1,0} - x_{1,e}) \frac{e^{-v_1 t_i} - 1}{v_1}$$

$$- b_1(x_{3,e} - x_{3,0}) \frac{e^{-v_3 t_i} - 1}{v_3} ; \qquad \text{(IV-47)}$$

In the same manner:

$$\varepsilon_{3,1} = \tilde{x}_{3,i} - x_{3,0} + b_3(x_{1,0} - x_{1,e}) \frac{e^{-v_1 t_i} - 1}{v_1}$$

$$+ a_3(x_{3,e} - x_{3,0}) \frac{e^{-v_3 t_i} - 1}{v_3} ; \; i=1,2,\ldots,N \qquad \text{(IV-48)}$$

The above model represented by Equations (IV-47) and (IV-48) will be called "Linear Exponential Model" because of its linearity with respect to the parameters of interest. Again, k_1, k_2, k_3, v_1, and v_3 are to be estimated simultaneously.

5. Nonlinear Polynomial Model II

The models discussed so far, fail to take into account the effect of all three parameters simultaneously. The error model for x_1 is expressed as a function of k_1 and k_3, whereas the error model for x_3 is expressed as a function of k_2 and k_3. In addition to that, the decoupling of v_1 and v_3

in the "Nonlinear Exponential Model I" limits the usefulness of this model, since one would not expect to obtain a unique set of parameters which will minimize the least-squares objective function in the region of interest.

In order to express the error models for x_1 and x_3 as functions of k_1, k_2, and k_3, the following approach is taken.

For convenience, Equations (IV-13) and (IV-14) are reproduced below:

$$x_1' = - a_1 x_1 + b_1 x_3 + k_1 \qquad \text{(IV-49)}$$

$$x_3' = b_3 x_1 - a_3 x_3 + K_2 k_2 \qquad \text{(IV-50)}$$

Differentiating Equation (IV-49) with respect to t yields:

$$x_1'' = a_1 x_1' + b_1 x_3' \qquad \text{(IV-51)}$$

Replacing x_3' in Equation (IV-51) by Equation (IV-50) yields:

$$x_1'' + a_1 x_1' = b_1(b_3 x_1 - a_3 x_3 + K_2 k_2) = F_1(\underline{x}:\underline{k}) \qquad \text{(IV-52)}$$

In the same manner:

$$x_3'' + a_3 x_3' = b_3(-a_1 x_1 + b_1 x_3 + k_1) = F_3(\underline{x}:\underline{k}) \qquad \text{(IV-53)}$$

The initial conditions of (IV-52) and (IV-53) are:

$$x_1(0) = x_{1,0}$$

$$x_3(0) = x_{3,0}$$

$$x_1'(0) = x_{1,0}' = - a_1 x_{1,0} + b_1 x_{3,0} + k_1 \qquad \text{(IV-54)}$$

$$x_3'(0) = x_{3,0}' = b_3 x_{1,0} - a_3 x_{3,0} + K_2 k_2$$

The solutions of Equations (IV-52) and (IV-53) with initial conditions given by Equation (IV-54) are:

$$x_1 = x_{1,0} + x_{1,0}'\left(\frac{1-e^{-a_1 t}}{a_1}\right) + \frac{1}{a_1}\int_0^t [1-e^{a_1(\xi-t)}]F_1(\underline{x}(\xi):\underline{k})d\xi \qquad \text{(IV-55)}$$

$$x_3 = x_{3,0} + x_{3,0}'\left(\frac{1-e^{-a_3 t}}{a_3}\right) + \frac{1}{a_3}\int_0^t [1-e^{a_3(\xi-t)}]F_3(\underline{x}(\xi):\underline{k})d\xi \qquad \text{(IV-56)}$$

Combining Equations (IV-55), (IV-56) and (IV-27), (IV-28) gives the following error model in discretized form:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - x_{1,0}'\left(\frac{1-e^{-a_1 t_i}}{a_1}\right) - \frac{b_1}{a_1}\{K_2 k_2 \int_0^{t_i} [1-e^{a_1(\xi-t_i)}]d\xi$$

$$+ b_3 \sum_{m=0}^{L} \hat{p}_m \int_0^{t_i} [1-e^{a_1(\xi-t_i)}]\xi^m d\xi$$

$$- a_3 \sum_{m=0}^{M} \hat{q}_m \int_0^{t_i} [1-e^{a_1(\xi-t_i)}]\xi^m d\xi\}; \qquad \text{(IV-57)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0} - x'_{3,0}\left(\frac{1-e^{-a_3 t_i}}{a_3}\right) - \frac{b_3}{a_3}\{k_1 \int_0^{t_i} [1-e^{a_3(\xi-t_i)}]d\xi$$

$$- a_1 \sum_{m=0}^{L} \hat{p}_m \int_0^{t_i} [1-e^{a_3(\xi-t_i)}]d\xi$$

$$+ b_1 \sum_{m=0}^{M} \hat{q}_m \int_0^{t_i} [1-e^{a_3(\xi-t_i)}]d\xi\}; \quad i=1,2,\ldots,N \qquad \text{(IV-58)}$$

Note that in the above model, both Equation (IV-57) and (IV-58) contain k_1, k_2, and k_3. This model will be called "Nonlinear Polynomial Model II".

6. Nonlinear Exponential Model II

Replacing x_1 and x_3 in $F_1(\underline{x}:\underline{k})$ by Equations (IV-39) and (IV-40) yields:

$$F_1(\underline{x}:\underline{k}) \tilde{=} b_1\{K_2 k_2 + b_3[x_{1,e} + (x_{1,0} - x_{1,e})e^{-v_1 t}]$$

$$- a_3[x_{3,e} + (x_{3,0} - x_{3,e})e^{-v_3 t}]\}$$

$$= b_1(K_2k_2 + b_3x_{1,e} - a_3x_{3,e})$$

$$+ b_1[b_3(x_{1,0} - x_{1,e})e^{-v_1t} - a_3(x_{3,0} - x_{3,e})e^{-v_3t}]$$

(IV-59)

Keeping in mind that:

$$K_2k_2 + b_3x_{1,e} - a_3x_{3,e} = 0 \ ,$$

Equation (IV-59) reduces to:

$$F_1(\underline{x}:\underline{k}) \tilde{=} b_1[b_3(x_{1,0} - x_{1,e})e^{-v_1t} - a_3(x_{3,0} - x_{3,e})e^{-v_3t}]$$

(IV-60)

In the same manner:

$$F_3(\underline{x}:\underline{k}) \tilde{=} - b_3[a_1(x_{1,0} - x_{1,e})e^{-v_1t} + b_1(x_{3,e} - x_{3,0})e^{-v_3t}]$$

(IV-61)

Combining Equations (IV-60) and (IV-61) with Equations (IV-55) and (IV-56) yields, after integration:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} - x'_{1,0}\left(\frac{1-e^{-a_1t_i}}{a_1}\right)$$

$$- \frac{b_1}{a_1}\left[b_3(x_{1,0} - x_{1,e})\left(\frac{1-e^{-v_1 t_i}}{v_1} + \frac{e^{-a_1 t_i} - e^{-v_1 t_i}}{a_1 - v_1}\right)\right.$$

$$\left. + a_3(x_{3,e} - x_{3,0})\left(\frac{1-e^{-v_3 t_i}}{v_3} + \frac{e^{-a_1 t_i} - e^{-v_3 t_i}}{a_1 - v_3}\right)\right] ; \qquad \text{(IV-62)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0} - x'_{3,0}\left(\frac{1-e^{-a_3 t_i}}{a_3}\right)$$

$$+ \frac{b_3}{a_3}\left[a_1(x_{1,0} - x_{1,e})\left(\frac{1-e^{-v_1 t_i}}{v_1} + \frac{e^{-a_3 t_i} - e^{-v_1 t_i}}{a_3 - v_1}\right)\right.$$

$$\left. + b_1(x_{3,e} - x_{3,0})\left(\frac{1-e^{-v_3 t_i}}{v_3} + \frac{e^{-a_3 t_i} - e^{-v_3 t_i}}{a_3 - v_3}\right)\right] ;$$

$$i=1,2,\ldots,N \qquad \text{(IV-63)}$$

Note that in the above model, both Equation (IV-62) and (IV-63) contain k_1, k_2, k_3, v_1, and v_3. This model will be called "Nonlinear Exponential Model II".

The approaches taken in developing the various error models above can be generalized to an n-component monomolecular reversible reaction system; in this case, the error model would consist of n-1 equations.

C. Generation of Data

1. Generation of Noise-Free Data

Data was generated by using the fourth-order Runge-Kutta integration scheme, with initial conditions:

$$x_{1,0} = 1.0$$

$$x_{2,0} = 0.0$$

$$x_{3,0} = 0.0$$

The k values were taken from Wei and Prater (30) who have considered the reaction between 1-butene, cis-2-butene, and trans-2-butene in specific:

$$k_{21} = 10.344 \quad ; \quad k_{12} = 4.623$$

$$k_{32} = 5.616 \quad ; \quad k_{23} = 3.371$$

$$k_{13} = 1.000 \quad ; \quad k_{31} = 3.724$$

With the terminology given by Equation (IV-12), the true values of parameters of interest are those ones given on the second column above.

Integration was continued until equilibrium conditions were met, although only the first twenty observations (excluding the initial conditions) were picked for estimation pur-

poses. Those are given in Table IV-1.

With the initial conditions and parameter values given above, the generated composition profile for x_1 is monotonically decreasing, whereas that for x_3 is monotonically increasing. The composition profile for x_3 passes through a maximum before reaching equilibrium. This is the reason for choosing x_1 and x_3 to be approximated by exponential functions, rather than x_2.

2. Generation of Noisy Data

Twenty sets of noisy observations were obtained by the addition of random numbers with Gaussian distribution to the true solutions for x_1 and x_3 using:

$$\tilde{x}_{1,ij} = x^*_{1,i} + \tilde{\varepsilon}_{ij} \; ; \qquad \text{(IV-64)}$$

$$\tilde{x}_{3,ij} = x^*_{3,i} + \tilde{\varepsilon}'_{ij} \; ; \quad i,j=1,2,\ldots,20 \qquad \text{(IV-65)}$$

where $x^*_{1,i}, x^*_{3,i}$ = true observations at $t = t_i$,

$\tilde{x}_{1,ij}, \tilde{x}_{3,ij}$ = noisy observations at $t = t_i$, for the jth run,

$\tilde{\varepsilon}_{ij}, \tilde{\varepsilon}'_{ij}$ = random numbers with Gaussian distribution, both having zero means and a standard deviation of 0.01.

The initial and equilibrium conditions were not subjected to noise. Thus the terms $x_{1,0}$, $x_{1,e}$, $x_{3,0}$, and $x_{3,e}$ encountered in the earlier sections should be interpreted

TABLE IV-1

NOISE-FREE OBSERVATIONS

t	x_1	x_3
0.000	1.000000	0.000000
0.025	0.715513	0.089021
0.050	0.531162	0.167940
0.075	0.410354	0.235654
0.100	0.330171	0.292515
0.125	0.276195	0.339559
0.150	0.239304	0.378070
0.175	0.213688	0.409355
0.200	0.195611	0.434626
0.225	0.182652	0.454951
0.250	0.173223	0.471246
0.275	0.166265	0.484279
0.300	0.161068	0.494683
0.325	0.157143	0.502977
0.350	0.154151	0.509581
0.375	0.151853	0.514836
0.400	0.150076	0.519014
0.425	0.148694	0.522334
0.450	0.147616	0.524971
0.475	0.146771	0.527066
0.500	0.146107	0.528729

as noise-free initial and equilibrium conditions.

D. Treatment of Data

Forsythe's method was used to fit polynomials in t to all the observation sets. The best-fit polynomial for each set was chosen according to the variance criterion described in Section G.2 of Chapter III. When evaluated at t=0, those polynomials did not yield the initial conditions ($x_{1,0} = 1.0$, $x_{3,0} = 0.0$) exactly. In order to ensure that the initial conditions were satisfied to an accuracy of five digits, a weight of 10,000 was given to both $x_{1,0}$ and $x_{3,0}$ in the Forsythe fitting procedure. Unit weights were assigned to the remaining twenty points.

The initial parameter guesses are shown in Table IV-2.

The weighting matrix used was:

$$\underline{W}_{(2N\times 2N)} = \begin{bmatrix} \underline{W}_{1(N\times N)} & \underline{0} \\ \underline{0} & \underline{W}_{3(N\times N)} \end{bmatrix} \qquad \text{(IV-66)}$$

where $$\underline{W}_{1(N\times N)} = \frac{1}{\sigma_1^2}\,\underline{I}_{(N\times N)} \qquad \text{(IV-67)}$$

$$\underline{W}_{3(N\times N)} = \frac{1}{\sigma_3^2}\,\underline{I}_{(N\times N)} \qquad \text{(IV-68)}$$

$$\underline{I}_{(N\times N)} = \text{the identity matrix.} \qquad \text{(IV-69)}$$

TABLE IV-2

INITIAL GUESSES OF THE PARAMETERS

	Polynomial Models	Exponential Models
$k_1^{(0)}$	5.0	5.0
$k_2^{(0)}$	5.0	5.0
$k_3^{(0)}$	5.0	5.0
$v_1^{(0)}$	---	10.0
$v_3^{(0)}$	---	7.0

For the noisy measurements, both σ_1 and σ_3 were set equal to 0.01. With these values, Equation (IV-66) reduces to:

$$\underline{W}_{(2N\times 2N)} = 1.0 \times 10^{-4}\ \underline{I}_{(2N\times 2N)} \qquad \text{(IV-70)}$$

In other words, equal weights were used in the minimization of the objective function, since it was known that both observations had the same error distribution.

For the noise-free measurements σ_1 and σ_3 were set equal to 1.0×10^{-4} somewhat arbitrarily.

E. Results and Discussion

1. Noise-Free Observations

For convenience, the true values of the parameters are reproduced below:

$$k_1 = 4.623\ ,\quad k_2 = 3.371\ ,\quad k_3 = 3.724$$

With the polynomial models, fifth, sixth, and seventh degree approximating polynomials for x_1 and x_3 were tried. The results are presented in Table IV-4. A study of these shows the effect of increasing the polynomial degree on the accuracies of the estimates. One should be cautious, though, in using polynomials with high degrees in the case of noisy observations.

Attempts to estimate the parameters using the Nonlinear

Exponential Model I failed. This could be atrributed to the fact that Equation (IV-44) contains only k_1, k_3, and v_3, and Equation (IV-45) contains only k_2, k_3, and v_1.

The Linear Exponential Model converged to a unique set of parameter estimates, but these were somewhat far from the true values.

Among the exponential models the most successful one was the Nonlinear Exponential Model II. In this model both Equation (IV-62) and Equation (IV-63) are functions of all the five parameters. Thus, the parameters are completely coupled.

One can conclude that the exponential models are not as successful as the polynomial models. This can be attributed to the lower flexibility of an exponential function of the form given by Equation (IV-39) or (IV-40) in approximating a given set of data. Once the initial and equilibrium conditions have been fixed, there is just one exponential parameter left to be estimated. In the case where a polynomial is used as an approximating function, the number of parameters to be determined is equal to the degree of the polynomial if the initial condition is fixed.

The results for noise-free measurements with the exponential models are presented in Table IV-3.

TABLE IV-3

PARAMETER ESTIMATES FROM NOISE-FREE OBSERVATIONS

	Model	
	Linear Exponential	Nonlinear Exponential II
$\hat{k}_1$	4.264	4.582
$\hat{k}_2$	8.306	3.094
$\hat{k}_3$	3.599	3.842

TABLE IV-4

PARAMETER ESTIMATES FROM NOISE-FREE OBSERVATIONS

Model	Nonlinear Polynomial I			Linear Polynomial			Nonlinear Polynomial II		
Degree of Approximating Polynomial	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$
5	4.609	3.353	3.746	4.542	3.321	3.780	4.594	3.308	3.760
6	4.620	3.367	3.729	4.603	3.360	3.737	4.616	3.356	3.733
7	4.622	3.370	3.725	4.618	3.369	3.727	4.621	3.367	3.726

2. Noisy Observations

Considering the relatively inferior results obtained with the exponential models, especially the linear exponential model, using the noise-free observations, it was felt that further testing of these models with noisy observations was unnecessary. For the polynomial models, the results of the individual runs from one to twenty are shown in Tables IV-6 and IV-8. The summarized statistical results are shown in Table IV-5, using the nomenclature given in Section D.2 of Chapter III.

Studying Table IV-5 the following conclusions are drawn:

(a) The variance estimates of the parameters are nearly the same with the three models. Based on this observation, the null hypothesis that the variance estimates of each parameter, obtained with different models come from populations with the same variance was tested. The results, obtained using an F-test for the homogeneity of variance, showed that this hypothesis can be accepted quite reasonably. From the nosie-free measurements, it is also known that the mean values of each parameter, obtained with different models, come from populations with the same mean. The above two points suggest that it is quite reasonable to assume that the parameter estimates obtained with the three different models come from the same population. Based on this assumption, the use of the linear polynomial model is strongly recommended, due to the simplicity of computation

TABLE IV-5

STATISTICAL RESULTS FROM NOISY OBSERVATIONS

	Model		
	Nonlinear Polynomial I	Linear Polynomial	Nonlinear Polynomial II
$\bar{k}_1$	4.592	4.502	4.562
$\bar{k}_2$	3.335	3.268	3.292
$\bar{k}_3$	3.748	3.812	3.769
$\tilde{s}^2_{k_1}$	0.0911	0.0654	0.0734
$\tilde{s}^2_{k_2}$	0.2338	0.2323	0.1975
$\tilde{s}^2_{k_3}$	0.1858	0.1766	0.1629
$\bar{s}^2_{k_1}$	0.0374	0.0102	0.0284
$\bar{s}^2_{k_2}$	0.0992	0.0406	0.0983
$\bar{s}^2_{k_3}$	0.0752	0.0297	0.0643
$\frac{(\tilde{s}^2_{k_1})^{1/2}}{\bar{k}_1}$	0.066	0.057	0.059
$\frac{(\tilde{s}^2_{k_2})^{1/2}}{\bar{k}_2}$	0.145	0.147	0.135
$\frac{(\tilde{s}^2_{k_3})^{1/2}}{\bar{k}_3}$	0.115	0.110	0.107

TABLE IV-6

INDIVIDUAL ESTIMATES

NONLINEAR POLYNOMIAL MODEL I

Run No.	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$	$\hat{s}^2_{k_1} \times 10$	$\hat{s}^2_{k_2} \times 10$	$\hat{s}^2_{k_3} \times 10$
1	4.801	3.801	3.419	0.375	1.097	0.824
2	4.326	3.180	3.969	0.300	0.914	0.647
3	4.295	2.897	4.124	0.289	0.814	0.604
4	4.548	3.397	3.825	0.349	1.067	0.766
5	4.562	3.232	3.969	0.315	0.802	0.635
6	5.085	4.101	2.928	0.464	1.399	1.093
7	4.533	3.377	3.622	0.339	1.023	0.757
8	4.459	3.025	3.985	0.323	0.895	0.685
9	4.624	3.381	3.720	0.353	1.021	0.763
10	5.012	3.533	3.540	0.387	0.913	0.793
11	4.624	2.818	4.217	0.296	0.741	0.585
12	4.411	2.830	3.975	0.300	0.735	0.599
13	4.512	3.348	3.612	0.330	0.962	0.721
14	4.489	3.370	3.808	0.349	1.138	0.795
15	5.327	4.744	2.619	0.559	1.912	1.389
16	4.183	2.993	4.206	0.275	0.839	0.577
17	4.177	2.650	4.432	0.270	0.750	0.545
18	4.508	3.021	3.943	0.318	0.831	0.662
19	4.721	3.417	3.495	0.357	0.946	0.766
20	4.891	3.592	3.550	0.388	1.036	0.835

TABLE IV-7

INDIVIDUAL ESTIMATES

LINEAR POLYNOMIAL MODEL

Run No.	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$	$\hat{S}^2_{k_1}$ x10	$\hat{S}^2_{k_2}$ x10	$\hat{S}^2_{k_3}$ x10
1	4.711	3.675	3.520	0.109	0.432	0.317
2	4.273	3.028	4.087	0.088	0.383	0.262
3	4.236	2.881	4.157	0.087	0.368	0.257
4	4.459	3.291	3.858	0.107	0.446	0.315
5	4.545	3.041	4.151	0.089	0.327	0.254
6	4.894	4.073	3.019	0.129	0.501	0.375
7	4.423	3.427	3.615	0.101	0.430	0.298
8	4.408	3.077	3.953	0.099	0.396	0.289
9	4.576	3.463	3.628	0.111	0.444	0.324
10	4.905	3.465	3.677	0.107	0.355	0.298
11	4.310	2.627	4.341	0.090	0.332	0.256
12	4.444	2.983	3.789	0.103	0.375	0.295
13	4.448	3.291	3.643	0.100	0.400	0.291
14	4.412	3.475	3.749	0.106	0.479	0.318
15	5.080	4.628	2.802	0.146	0.618	0.434
16	4.161	2.859	4.308	0.081	0.361	0.240
17	4.068	2.515	4.559	0.081	0.353	0.239
18	4.414	2.981	3.993	0.093	0.350	0.266
19	4.607	3.296	3.587	0.106	0.389	0.304
20	4.664	3.280	3.809	0.106	0.390	0.304

TABLE IV-8

INDIVIDUAL ESTIMATES

NONLINEAR POLYNOMIAL MODEL II

Run No.	$\hat{k}_1$	$\hat{k}_2$	$\hat{k}_3$	$\hat{S}^2_{k_1} \times 10$	$\hat{S}^2_{k_2} \times 10$	$\hat{S}^2_{k_3} \times 10$
1	4.780	3.803	3.404	0.311	1.488	0.920
2	4.293	3.226	3.972	0.316	1.157	0.692
3	4.301	2.895	4.124	0.289	0.665	0.490
4	4.484	3.308	3.845	0.288	1.153	0.699
5	4.507	3.184	4.083	0.363	0.983	0.703
6	4.965	3.784	3.091	0.209	1.200	0.717
7	4.555	3.140	3.679	0.215	0.649	0.456
8	4.475	3.025	3.967	0.262	0.651	0.478
9	4.616	3.318	3.700	0.248	0.926	0.608
10	5.041	3.408	3.623	0.249	0.754	0.603
11	4.346	2.925	4.186	0.322	0.813	0.567
12	4.397	2.834	3.942	0.287	0.660	0.507
13	4.495	3.318	3.604	0.257	1.010	0.635
14	4.486	3.188	3.867	0.226	0.713	0.471
15	5.157	4.712	2.693	0.342	2.151	1.188
16	4.147	2.976	4.250	0.328	0.980	0.613
17	4.210	2.778	4.369	0.298	0.588	0.441
18	4.543	2.958	3.947	0.268	0.558	0.456
19	4.658	3.467	3.466	0.283	1.222	0.766
20	4.787	3.588	3.564	0.318	1.343	0.856

involved, since no iteration is required.

(b) The sensitivity of the parameters to observation errors goes in decreasing order from k_2 to k_3 and k_1. It should be noted that this observation would not generally be valid if initial conditions different than the ones in this analysis were used. As pointed out by Wei and Prater (30) and Donnelly and Quon (9), different initial conditions would lead to different parameter sensitivities, and certain initial conditions would not lead to any estimates at all. Therefore, the dependence of the parameter estimates to the experimental conditions should always be investigated in order to obtain a reasonable degree of reliability.

(c) The actual variances of the parameter estimates, $\tilde{S}^2_{k_i}$; i=1,2,3, are larger than the averages of the individual parameter estimates, $\bar{S}^2_{k_i}$; i=1,2,3. This is a result of the fact that the coefficients of the approximating polynomials are not considered as random numbers during the estimation of the parameters. Thus the confidence obtained in the parameter estimates appears to be higher than it actually should be. A suggestion to obtain more realistic confidence intervals will be made in Section G of this chapter.

F. Time Requirements

1. Nonlinear Polynomial Model I

Average time required : 12 seconds/iteration.

Average number of iterations : 5 (per run).

2. Linear Polynomial Model

Computing time was very short in this case due to the linearity of the model with respect to the parameters.

3. Nonlinear Polynomial Model II

Average time required : 21 seconds/iteration.

Average number of iterations : 5 (per run).

The time required for the estimation of the coefficients of the approximating polynomial was about 10 seconds per run.

G. Comments on the Polynomial Models

(a) Both the nonlinear and linear polynomial models used in the estimation of k_1, k_2, and k_3 are discrete error models. If $\tilde{x}_1$ and $\tilde{x}_3$ are replaced by their approximating polynomials, the resulting models will be continuous in t. With this choice, the linear polynomial model takes the following form:

$$\varepsilon_1(t) = \sum_{m=0}^{L} \hat{p}_m t^m - x_{1,0} - k_1 t + a_1 \sum_{m=0}^{L} \frac{\hat{p}_m}{m+1} t^{m+1}$$

$$- b_1 \sum_{m=0}^{M} \frac{\hat{q}_m}{m+1} t^{m+1} \qquad \text{(IV-71)}$$

$$\varepsilon_3(t) = \sum_{m=0}^{M} \hat{q}_m t^m - x_{3,0} - K_2 k_2 t - b_3 \sum_{m=0}^{L} \frac{\hat{p}_m}{m+1} t^{m+1}$$

$$+ a_3 \sum_{m=0}^{M} \frac{\hat{q}_m}{m+1} t^{m+1} \qquad \text{(IV-72)}$$

After rearranging, the above equations can be written as:

$$\varepsilon_1(t) = - x_{1,0} - k_1 t + \sum_{m=0}^{L} (1 + \frac{a_1}{m+1} t)\hat{p}_m t^m$$

$$- b_1 \sum_{m=0}^{M} \frac{\hat{q}_m}{m+1} t^{m+1} \qquad \text{(IV-73)}$$

$$\varepsilon_3(t) = - x_{3,0} - K_2 k_2 t - b_3 \sum_{m=0}^{L} \frac{\hat{p}_m}{m+1} t^{m+1}$$

$$+ \sum_{m=0}^{M} (1 + \frac{a_3}{m+1} t)\hat{q}_m t^m \qquad \text{(IV-74)}$$

With this continuous error model, the least-squares objective function is expressed as:

$$S = \int_0^{t_f} [\frac{1}{\sigma_1^2} \varepsilon_1^2(t) + \frac{1}{\sigma_3^2} \varepsilon_3^2(t)]dt \qquad \text{(IV-75)}$$

A natural choice for t_f would be t_N, i.e., the time at which the last measurements of x_1 and x_3 were taken.

Now one can set the derivative of S with respect to k_1, k_2, and k_3 equal to zero and can solve the resulting expressions for these parameters only as functions of the coefficients of the approximating polynomials. An estimate of the expected values and variances of these coefficients would readily be available from the original fitting procedure. One can then use relationships similar to those given

by Equations (III-27) and (III-28) in Section F of Chapter III to obtain confidence intervals for the parameters, which would be more reliable than those given by the linear polynomial model itself.

(b) The discussion would not be complete without a passing reference to the moment method. For convenience, Equations (IV-13) and (IV-14) are reproduced below:

$$x_1' = - a_1 x_1 + b_1 x_3 + k_1 \qquad \text{(IV-76)}$$

$$x_3' = b_3 x_1 - a_3 x_3 + K_2 k_2 \qquad \text{(IV-77)}$$

Replacing x_1 and x_3 by their approximating polynomials, the following error model is obtained:

$$\varepsilon_1(t) = x_1' + a_1 \sum_{m=0}^{L} \hat{p}_m t^m - b_1 \sum_{m=0}^{M} \hat{q}_m t^m - k_1 \qquad \text{(IV-78)}$$

$$\varepsilon_3(t) = x_3' - b_3 \sum_{m=0}^{L} \hat{p}_m t^m + a_3 \sum_{m=0}^{M} \hat{q}_m t^m - K_2 k_2 \qquad \text{(IV-79)}$$

Since the estimation of three parameters is desired, the moment conditions require that:

$$\int_0^{t_f} \left[\frac{1}{\sigma_1^2} \varepsilon_1^2(t) + \frac{1}{\sigma_3^2} \varepsilon_3^2(t)\right] t^j dt = 0; \quad j=0,1,2 \qquad \text{(IV-80)}$$

With this method too, the sensitivity of the parameters to

observation noise can be estimated as explained in Part (a).

Note that by expressing the error model in continuous form, one puts his whole confidence on the expected values of the polynomial coefficients, and does not worry about the experimental observations any longer. Thus, one might consider the discrete error models which are expressed in terms of experimental observations to be more realistic. The advantage of the continuous models is that they lend themselves to subsequent statistical analysis concerning the estimates of the parameters. It should be noted that this is restricted to systems of linear differential equations, or nonlinear differential equations which can be expressed in self-adjoint form, as encountered in Chapter III.

H. Others' Approaches

Wei and Prater (30) have studied the problem considered in this chapter and a family of related problems in considerable depth, and have come up with a method which makes use of the "straight-line reaction path". They construct examples in which the set of parameters estimated from a single reaction curve will reproduce the original data adequately, but will give quite different curves than those expected when different initial conditions are used. Their suggestion for overcoming this inconsistency is either to run the original experiments with widely differing initial conditions so that most of the reaction simplex will be covered, or to locate the straight-line reaction paths, which, they consider easier.

It should be noted that this approach also necessitates the running of more than one experiment to locate the straight-line reaction path; once this has been done, no use is made of the data obtained prior to that stage. In short, their approach is one of a design of an experiment, rather than being an approach to the treatment of a specific set of data.

In their work, attention has also been drawn to the hazards of using curve-fitting techniques for cases in which more than one exponential term is involved in the expression for the general solution. The model criticized is one obtained from the general solution to a set of linear differential equations, which, in the case of a three component system reduces to:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - c_{1,0} - c_{1,1}e^{-\lambda_1 t_i} - c_{1,2}e^{-\lambda_3 t_i}; \qquad \text{(IV-81)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - c_{3,0} - c_{3,1}e^{-\lambda_1 t_i} - c_{3,2}e^{-\lambda_3 t_i}; \qquad \text{(IV-82)}$$

$$i=1,2,\ldots,N$$

Assuming that the initial conditions are known exactly, as has been done before, the following relationships hold:

$$x_{1,0} = c_{1,0} + c_{1,1} + c_{1,2} \qquad \text{(IV-83)}$$

$$x_{3,0} = c_{3,0} + c_{3,1} + c_{3,2} \qquad \text{(IV-84)}$$

so that:

$$\varepsilon_{1,i} = \tilde{x}_{1,i} - x_{1,0} + c_{1,1}(1 - e^{-\lambda_1 t_i}) + c_{1,2}(1 - e^{-\lambda_3 t_i}); \qquad \text{(IV-85)}$$

$$\varepsilon_{3,i} = \tilde{x}_{3,i} - x_{3,0} + c_{3,1}(1 - e^{-\lambda_1 t_i}) + c_{3,2}(1 - e^{-\lambda_3 t_i}); \qquad i=1,2,\ldots,N \qquad \text{(IV-86)}$$

Note the close resemblance between this model and the Linear Exponential Model described by Equations (IV-47) and (IV-48).

Wei and Prater have also given the analytical solution for the three-component reaction system described by Equations (IV-1) to (IV-6) as a function of k's. In view of that fact, one might be tempted to use this analytical model for the purpose of estimating the parameters. Examination of the solution, though, leads one to conclude that it depends on the parameters in a rather complicated manner; the possibility of using this analytical model is, thus, discarded.

Donnelly and Quon (9) have attacked the same problem using quasilinearization. They have used different combinations of data obtained with seven different initial conditions. Naturally, the best results were obtained when all the seven data sets were used simultaneously. They report that using

only one data set generated with the initial conditions used in this chapter leads to acceptable results.

CHAPTER V

A NON-ISOTHERMAL DECOMPOSITION PROBLEM

A. Statement of the Problem

The pyrolysis of ethane in the temperature range 1200 to 1700°F is represented by:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (V\text{-}1)$$

The reaction is carried out in a steel tube with no internal obstructions (e.g., catalyst), contained in a furnace. In the development of the relevant differential equations describing the composition and temperature profiles along the length of the reactor, the following assumptions will be made:

(a) Any pressure drop along the length of the tube can be ignored,

(b) There is complete mixing in the radial direction and no mixing in the axial direction (i.e., the flow is governed by plug-flow behavior),

(c) No temperature gradient exists in the radial direction,

(d) Ideal gas law holds.

With the above assumptions, the differential equations

obtained by setting up material and energy balance equations over a differential volume element of the reactor are (5):

$$\frac{dz}{dx} = \frac{3600\ A'P}{n_0 R}\ \frac{k}{T_R}\ \frac{1-z}{1+z} \qquad \text{(V-2)}$$

$$\frac{dT_R}{dx} = \frac{\frac{q}{n_0} - \Delta H_R \frac{dz}{dx}}{(1-z)c_{p_A} + z(c_{p_B} + c_{p_C})} \qquad \text{(V-3)}$$

where A' = cross sectional area of tube, sq. ft.,

c_p = specific heat of C_2H_6, C_2H_4 and H_2 corresponding to the subscripts A, B, and C, BTU/lbmole-°R,

k = reaction rate constant, sec^{-1},

n_0 = feed rate of ethane, lbmoles/hr,

P = mean pressure inside the reactor, psia,

q = heat input from furnace, BTU/hr-ft. of tube,

R = ideal gas constant, 10.73 psia-cu. ft./lbmole-°R,

T_R = measure of absolute temperature, °R,

x = measure of the distance from the reactor inlet, ft.,

z = measure of the fraction of ethane converted to ethylene and hydrogen,

ΔH_R = heat of reaction, BTU/lbmole.

The purpose of the original problem given in (5) is to generate the conversion and temperature profiles along the

reactor, given the following information:

$$k = 5.764 \times 10^{16} e^{-\frac{41,310}{T_K}}, \text{ sec}^{-1} \qquad \text{(V-4)}$$

and

$$\underline{c_p, \text{ cal/gmole-°K}}$$

$$C_2H_6 : 3.75 + 35.7 \times 10^{-3} T_K - 10.12 \times 10^{-6} T_K^2$$

$$C_2H_4 : 5.25 + 24.2 \times 10^{-3} T_K - 6.88 \times 10^{-6} T_K^2 \qquad \text{(V-5)}$$

$$H_2 : 7.00 - 38.5 \times 10^{-5} T_K - 0.60 \times 10^{-6} T_K^2$$

$$\Delta H_R = 1.8[32,732 + 8.50(T_K - 298) - 5.942 \times 10^{-3}(T_K^2 - 298^2)$$

$$+ 1.28 \times 10^{-6}(T_K^3 - 298^3)], \text{ BTU/lbmole} \qquad \text{(V-6)}$$

where T_K is the measure of the absolute temperature in °K.

As seen from (V-4), k in general can be expressed as:

$$k = k_1 e^{-\frac{k_2}{T_K}} . \qquad \text{(V-7)}$$

Let

$$k_1 = a_1 \times 10^{-5} \qquad \text{(V-8)}$$

$$k_2 = a_2 \times 10^{3} \qquad \text{(V-9)}$$

Combining Equations (V-2), (V-7), (V-8), and (V-9) gives:

$$\frac{dz}{dx} = Da_1 \frac{e^{-\frac{1800}{T_R} a_2}}{T_R} \frac{1-z}{1+z} \qquad \text{(V-10)}$$

where $D = \frac{3600\ A'P}{n_0 R} \times 10^{15}$. (V-11)

In the derivation of Equation (V-10), use has also been made of the following relationship:

$$T_K = \frac{T_R}{1.8} \qquad \text{(V-12)}$$

The initial conditions for the differential equations described by (V-10) and (V-3) are:

$$z = z_0 \ ; \qquad \text{(V-13)}$$

and

$$T_R = T_{R,0} \ ; \quad \text{at} \quad x=0. \qquad \text{(V-14)}$$

The estimation problem can now be posed as one of estimating a_1 and a_2 given the thermodynamic information supplied by (V-5) and (V-6), together with the conversion and temperature measurements along the length of the reactor. In other words, given the thermodynamic information, the estimation of the parameters related to kinetic effects is desired.

B. Error Model

The general approach in the previous problems was to introduce some approximating function into the differential equations and try to estimate both the coefficients involved in the approximating functions and the original parameters simultaneously. Specifically, when ordinary polynomials in x are considered as approximating functions, the approach mentioned above will not be practical due to the resulting expressions for which the analytical integrals do not exist. This is the most general case encountered in the estimation of parameters from systems of ordinary differential equations. Below, a new approach to deal with this case will be described.

Suppose the noisy conversion and temperature measurements have been smoothed by:

$$P(x) = \sum_{m=0}^{L} \hat{p}_m x^m \qquad \text{(V-15)}$$

and

$$R(x) = \sum_{m=0}^{M} \hat{r}_m x^m \ , \qquad \text{(V-16)}$$

respectively. L and M are the optimum polynomial degrees chosen in accordance with the minimum variance criterion described previously.

Now, integration of Equations (V-10) and (V-13) gives:

$$\varepsilon_{z,i} = \tilde{z}_i - z_0 - Da_1 \int_0^{x_i} \frac{1}{T} e^{-\frac{1800}{T} a_2} \frac{1-z}{1+z} dx;$$

$$= \tilde{z}_i - z_0 - Da_1 \int_0^{x_i} f(T,z:a_2)dx; \qquad (V\text{-}17)$$

$$\varepsilon_{T,i} = \tilde{T}_i - T_0 - \int_0^{x_i} \frac{\frac{q}{n_o} - \Delta H_R Da_1 f(T,z:a_2)}{(1-z)c_{p_A} + z(c_{p_B} + c_{p_C})} dx; \qquad (V\text{-}18)$$

$$i=1,2,\ldots,N$$

where T_R has been replaced by T for notational simplicity. $\tilde{z}_i$ and $\tilde{T}_i$ are the observed values of z and T at $x = x_i$.

Substitution of Equations (V-15) and (V-16) into Equations (V-17) and (V-18) yields:

$$\varepsilon_{z,i} = \tilde{z}_i - z_0 - Da_1 \int_0^{x_i} \frac{1}{R(x)} e^{-\frac{1800}{R(x)} a_2} \frac{1-P(x)}{1+P(x)} dx$$

$$= \tilde{z}_i - z_0 - Da_1 \int_0^{x_i} \phi(x:a_2)dx; \qquad (V\text{-}19)$$

$$\varepsilon_{T,i} = \tilde{T}_i - T_0 - \int_0^{x_i} \frac{\frac{q}{n_0} - \Delta H_R Da_1 \phi(x:a_2)}{[1-P(x)]c_{p_A} + P(x)(c_{p_B} + c_{p_C})} dx$$

$$= \tilde{T}_i - T_0 - \int_0^{x_i} \psi(x:a_1,a_2)dx; \quad i=1,2,\ldots,N \qquad (V\text{-}20)$$

In interpreting Equation (V-20) it should be kept in mind that ΔH_R, c_{p_A}, c_{p_B}, and c_{p_C} are now functions of R(x), although this dependence has not been shown explicitly, for

notational simplicity.

The least-squares objective function to be minimized is:

$$S = \sum_{i=1}^{N} \left(\frac{1}{\sigma_z^2} \varepsilon_{z,i}^2 + \frac{1}{\sigma_T^2} \varepsilon_{T,i}^2 \right) \qquad (V\text{-}21)$$

where σ_z^2 and σ_T^2 are estimates of the variances of the conversion and temperature measurements.

Note that the integrations required for evaluating the model errors and the sensitivity coefficients $\frac{\partial \varepsilon_z}{\partial a_j}\Big|_{x=x_i}$, $\frac{\partial \varepsilon_T}{\partial a_j}\Big|_{x=x_i}$; i=1,2,...,N; j=1,2, cannot be evaluated analytically. Instead, the integrands can be evaluated at a certain number of points, with the subsequent application of a quadrature formula or a simple formula such as Simpson's rule or the trapezoidal rule. The application of a quadrature formula usually requires the evaluation of the integrands at points other than those at which data was taken. In order to apply such a formula, $\tilde{z}$ and $\tilde{T}$ should be replaced by P(x) and R(x), so that the error model and the sensitivity coefficients are now continuous in x. A much simpler procedure would be to evaluate the integrands at the points at which data was taken, i.e., x_i; i=1,2,...,N, with the subsequent application of Simpson's rule or the trapezoidal rule. Obviously, the integration formulae used and the number of points at which the integrands are evaluated have an effect on the accuracies of the numerical integrals obtained. Nevertheless, it should be kept in mind that, no matter how accurate the integrals

are, the parameter estimates will be dependent on the coefficients of the approximating polynomials used. Thus, too much accuracy in integration, which in turn means an increase in computing time, would not be justified.

C. Generation of Data

1. Generation of Noise-Free Data

For the generation of the numerical solution the information given in the previous pages was used. The remaining operating variables are listed below:

$z_0 = 0$

$T_0 = 1460°R$

$D_i = 4.026$ in (inside diameter of tube)

$\frac{q}{\pi D_i} = 5000$ BTU/hr-sq-ft. (of the inside of tube)

$P = 30$ psia

$n_0 = 60$ lbmoles/hr.

With those values and initial conditions Equations (V-2) and (V-3) were integrated numerically, using step sizes of 1.0, 0.5, and 0.1 ft. For each step size nearly identical results were obtained, which were printed out at 25 ft. intervals. Smaller step sizes were not tried due to time limitations and possible round-off errors which might become significant with the increasing number of calculations. The first 35 points obtained using a step size of 0.1 ft. were taken to

represent the noise-free measurements. These are presented in Table V-1.

2. Generation of Noisy Data

Twenty sets of noisy observations were obtained by the addition of random numbers with Gaussian distribution to the solution generated by numerical integration, using:

$$\tilde{z}_{ij} = z_i^* + \tilde{\varepsilon}_{z,ij}; \quad i=1,2,\ldots,34; \; j=1,2,\ldots,20 \qquad \text{(V-22)}$$

$$\tilde{T}_{ij} = T_i^* + \tilde{\varepsilon}_{T,ij}; \quad i=0,1,\ldots,34; \; j=1,2,\ldots,20 \qquad \text{(V-23)}$$

where z_i^*, T_i^* = true observations of z and T at $x = x_i$,

$\tilde{z}_{ij}, \tilde{T}_{ij}$ = noisy observations of z and T at $x = x_i$ for the jth run.

$\tilde{\varepsilon}_{z,ij}, \tilde{\varepsilon}_{T,ij}$ = random numbers with Gaussian distribution, zero mean, and standard deviations of 0.01 and 5.0, respectively.

As seen from Equation (V-22), the initial value of z was not subjected to noise.

D. Treatment of Data

Forsythe's method was used in fitting polynomials in x to all the observation sets. Comparison of variances corresponding to different polynomial degrees, led to the choice of fifth degree approximating polynomials for both z and T. In order to ensure that $z_0 = 0$ to an accuracy of five

digits, a weight of 10,000 was given to z_0 in the fitting procedure. Unit weights were assigned to the remaining points. In fitting polynomials to the temperature measurements, unit weights were assigned to all the 35 data points.

The model errors and sensitivity coefficients were evaluated at the 35 original points at which data was taken, using the trapezoidal rule for integration.

The initial parameter guesses were:

$$a_1^{(0)} = 40.0, \quad a_2^{(0)} = 40.0.$$

The weighting matrix used was:

$$\underline{W}_{(2N\times 2N)} = \begin{bmatrix} \underline{W}_{z(N\times N)} & \underline{0}_{(N\times N)} \\ \underline{0}_{(N\times N)} & \underline{W}_{T(N\times N)} \end{bmatrix} \tag{V-24}$$

where $$\underline{W}_{z(N\times N)} = \frac{1}{\sigma_z^2}\,\underline{I}_{(N\times N)} \tag{V-25}$$

$$\underline{W}_{T(N\times N)} = \frac{1}{\sigma_T^2}\,\underline{I}_{(N\times N)} \tag{V-26}$$

$$\underline{I}_{(N\times N)} = \text{the identity matrix.} \tag{V-27}$$

For the noisy observations σ_z and σ_T were set equal to 0.01 and 5.0, respectively. For the noise-free observations, they were set equal to 1.0×10^{-4} and 0.1, somewhat arbitrarily.

TABLE V-1

NOISE-FREE OBSERVATIONS

x,ft.	T,°R	z
0.0	1660.000	0.000000
25.0	1734.292	0.001368
50.0	1795.394	0.008165
75.0	1830.223	0.026991
100.0	1843.615	0.055922
125.0	1849.211	0.088562
150.0	1852.936	0.122093
175.0	1856.285	0.155802
200.0	1859.587	0.189531
225.0	1862.919	0.223243
250.0	1866.303	0.256927
275.0	1869.753	0.290577
300.0	1873.280	0.324188
325.0	1876.895	0.357753
350.0	1880.612	0.391266
375.0	1884.445	0.424720
400.0	1888.412	0.458106
425.0	1892.532	0.491415
450.0	1896.828	0.524635
475.0	1901.327	0.557754
500.0	1906.062	0.590754
525.0	1911.071	0.623616
550.0	1916.403	0.656317
575.0	1922.117	0.688827
600.0	1928.291	0.721106
625.0	1935.022	0.753107
650.0	1942.442	0.784764
675.0	1950.729	0.815986
700.0	1960.136	0.846647
725.0	1971.030	0.876564
750.0	1983.973	0.905451
775.0	1999.879	0.932849
800.0	2020.323	0.957957
825.0	2048.206	0.979297
850.0	2088.804	0.994154

E. Results and Discussion

1. Noise-Free Observations

For convenience, the true values of the parameters are reproduced below:

$$a_1 = 57.64, \quad a_2 = 41.31$$

Fifth, sixth, and seventh degree polynomials were tried as approximating functions. The results are presented in Table V-2.

Studying Table V-2 shows that the estimates of a_1 are somewhat dependent on the degree of the approximating polynomial used, whereas the estimates of a_2 are relatively insensitive to the degree of the approximating polynomial.

2. Noisy Observations

The results of the individual runs from one to twenty are shown in Table V-4. The summarized results are shown in Table V-3.

Studying Tables V-3 and V-4, the following conclusions are drawn:

(a) The estimates of a_1 are quite sensitive to observation errors, whereas the estimates of a_2 are reasonably stable.

(b) For each run, an increase in $\hat{a}_1$ is accompanied by an increase in $\hat{a}_2$.

(c) The variance estimates of a_1 are quite sensitive

to the observation errors, and vary in proportion to $\hat{a}_1$ (and $\hat{a}_2$) from run to run, whereas the variance estimates of a_2 are quite stable.

(d) The actual variances of the parameter estimates, $\hat{S}^2_{a_1}$ and $\hat{S}^2_{a_2}$, are larger than the averages of the individual parameter estimates, $\bar{S}^2_{a_1}$ and $\bar{S}^2_{a_2}$.

Conclusion (b) was directly supported by the high positive values of the correlation coefficient $\rho(a_1,a_2)$ observed during the individual least-squares runs. The correlation coefficient is defined by:

$$\rho(a_1,a_2) = \frac{\text{cov}(a_1,a_2)}{\hat{\sigma}^2_{a_1}\ \hat{\sigma}^2_{a_2}} \qquad \text{(V-28)}$$

where $\text{cov}(a_1,a_2)$ is the estimate of the covariance of a_1 and a_2.

It should be noted that the trends pointed out in Conclusions (a) to (c) emerge as a result of the characteristics of the system, i.e., the structure of the equations describing the system. Once the system is fixed by these equations, there is nothing that can be done to improve the results, no matter what kind of estimation technique is used, unless new experiments are run under more favorable conditions. Conclusion (d), on the other hand, can be attributed to the use of the approximating polynomials whose coefficients are treated as constants, rather than random variables.

TABLE V-2

PARAMETER ESTIMATES FROM NOISE-FREE OBSERVATIONS

Degree of Approximating Polynomial	$\hat{a}_1$	$\hat{a}_2$
5	48.18	41.12
6	60.28	41.36
7	58.05	41.32

TABLE V-3

STATISTICAL RESULTS FROM NOISY OBSERVATIONS

$\bar{a}_1$	40.39
$\bar{a}_2$	40.66
$\tilde{s}^2_{a_1}$	858.6
$\tilde{s}^2_{a_2}$	0.6762
$\frac{(\tilde{s}^2_{a_1})^{1/2}}{\bar{a}_1}$	0.725
$\frac{(\tilde{s}^2_{a_2})^{1/2}}{\bar{a}_2}$	0.020

TABLE V-4

INDIVIDUAL ESTIMATES

Run No.	$\hat{a}_1$	$\hat{a}_2$	$\hat{S}^2_{a_1}$	$\hat{S}^2_{a_2} \times 10^2$
1	29.40	40.60	7.24	0.918
2	6.53	38.99	0.33	0.851
3	19.76	40.20	3.18	0.894
4	17.83	40.05	2.61	0.897
5	76.41	41.60	49.59	0.930
6	22.89	40.33	4.24	0.884
7	61.93	41.38	31.54	0.901
8	29.76	40.62	7.75	0.959
9	53.11	41.22	22.96	0.892
10	22.49	40.33	4.13	0.894
11	7.21	39.10	0.42	0.881
12	37.82	40.91	11.75	0.901
13	95.15	41.82	81.85	0.990
14	40.91	40.92	13.65	0.892
15	41.22	41.00	13.62	0.880
16	72.77	41.57	43.60	0.903
17	111.46	42.02	100.89	0.890
18	15.58	39.90	1.87	0.840
19	24.65	40.42	4.67	0.841
20	20.91	40.23	3.32	0.831

F. Time Requirements

Convergence was reached in 4 to 5 iterations per run on the average. The computing time required was 19 seconds per iteration. Polynomial fitting to the observations took about 13 seconds per data set.

G. Comments on the Error Model

With the error model discussed in previous pages on hand, one has various options in carrying out the integrations necessary to evaluate the model errors and sensitivity coefficients. As noted previously, the model errors and sensitivity coefficients were evaluated at 35 equally spaced points along the length of the reactor. Integration at a certain point was carried out making use of the integrand values at the previous points already calculated. By studying the profile of these integrands along the x axis (distance from the reactor inlet), one could decide to redistribute the points at which the integrands should be evaluated. Thus, more evaluations would be made in regions where the slopes of the integrands are relatively large. Still another possibility would be to evaluate the model errors and sensitivity coefficients at points other than those at which the observations were made, in addition to these. This would seem to be especially useful when the number of observations is small. However, one should not overlook the fact that, in this case, those values predicted by the approximating polynomial, rather than those actually observed, are used in

the evaluation of the model errors. Since the number of observations is small, one's confidence in the coefficients of the approximating polynomials would be relatively small, with the consequence that one's confidence in the values of the resulting integrals would be small, no matter how exact the integration scheme is. This limitation should always be kept in mind while estimating the reliability of the parameter estimates.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In this study, semi-empirical models have been developed by introducing approximating functions into the integral transforms of the differential equations describing the system under study. In specific, ordinary power polynomials and exponential functions, expressed in terms of the independent variable, have been considered. The former have been found to be more flexible in approximating a given set of observations. Moreover, they possess the desirable property that they can be used in approximating any kind of observation set, regardless of the theoretical predictions about the shape of the profile of observations versus the independent variable. In some cases, however, it would be advantageous to use the knowledge about the theoretical predictions; if, say, theory predicts observations which will vary periodically with changes in the independent variable, then periodic functions of some kind should be considered as candidates for approximating functions. For cases where such trends are not expected, as was the case with the problems studied in this work, the use of ordinary power polynomials would prove of great advantage.

Almost no numerical difficulties were encountered with

the initial parameter guesses picked prior to estimation. If the initial guesses do not lead to converging results, the data perturbation scheme proposed by Donnelly and Quon (9) can be incorporated into the estimation algorithm.

The main goal of reducing the computation time due to integrations involved has been reached, not without a cost, however; the main problem now, is the difficulty encountered in establishing proper confidence intervals for the parameter estimates. Once the observations have been approximated by some functions, the parameters in these functions are considered to be constants for the rest of the computation. When the differential equations involved are linear, it is possible to express some parameters as functions of the parameters which appear in the approximating functions. Subsequently, confidence limits for the former can be established from a knowledge of the statistics of the latter. For nonlinear differential equations, which represent more realistic situations, this kind of analysis is not possible. Therefore, the development of a general approach which would consider the parameters in the approximating functions as random variables with known statistics, and carry out the subsequent estimation accordingly, would be very desirable.

In the approach developed in this work, systems consisting of only two simultaneous differential equations at the maximum have been considered. Another point of interest would be the investigation of the applicability of this approach to larger systems of differential equations.

NOMENCLATURE

CHAPTER I

Alphabetic

$\underline{a}$	p-vector of unknown parameters in the model
$f(y,x:\underline{a})$	function, defined by Equation (I-1)
$\underline{G}$	Nxp matrix of sensitivity coefficients
$g(x:\underline{a})$	function, defined by Equation (I-3)
N	number of data points per run
p	number of unknown parameters in the model
$\underline{R}$	pxp matrix, defined by Equation (I-4)
S	objective function to be minimized, a function of $\underline{\varepsilon}^T\underline{\varepsilon}$
v	p-vector, $\{\frac{\partial s}{\partial a_j}\ ;\ j=1,2,\ldots,p\}$
x,x_0	independent variable and its initial value
y,y_0	dependent variable and its initial value
$\underline{\tilde{y}}$	N-vector of observed values of y
$\underline{\hat{y}}$	N-vector of predicted values of y by the algorithm

Greek

$\underline{\delta}$	p-vector of corrections to the current values of the parameters
$\underline{\varepsilon}$	N-dimensional vector of model errors ($= \underline{\tilde{y}} - \underline{\hat{y}}$)

λ	a scaler determining step length

CHAPTER II

Alphabetic

$\underline{a}$	p-vector of unknown parameters in the original model
$\underline{b}, \hat{\underline{b}}$	q-vectors of coefficients of the approximating function and their least-squares estimates
$\underline{c}$	Vector with dimension smaller than p+q, obtained by combining the components of $\underline{a}$ and $\underline{b}$ in a manner determined by the specific problem on hand
$F(x,\xi:\underline{a})$	Green's function for the initial value problem
$f(y,v,x)$	a function
$G(x,\xi:\underline{a})$	Green's function for the boundary value problem
$h(y,x:\underline{a})$	a function
N	number of data points per run
$p(x:\underline{a})$	function, defined by Equation (II-5)
p	number of unknown parameters in the original model
q	number of coefficients of the approximating function
r	constant appearing in the first boundary condition
S	objective function to be minimized
s	constant appearing in the second boundary condition
$u(x:\underline{a})$	a function
$v(x:\underline{a})$	a function
x	independent variable
x_0, x_f	initial and final values of x

$y, \tilde{y}_i$	dependent variable and its observed value at $x=x_i$
$z(\nu,\eta,x:\underline{a})$	function, defined by Equation (II-4)

Greek

$\varepsilon_i, \varepsilon(x)$	discrete and continuous model errors
η	value of $y'(x)$ at $x=x_0$
μ_1, μ_2	constants appearing in the boundary conditions
ν	value of $y(x)$ at $x=x_0$
ξ	dummy variable, used for integration
ρ_1, ρ_2	constants appearing in the boundary conditions
$\phi(x:\underline{b})$	function approximating the observations of y
$\psi(x:\underline{a},\underline{b})$	function obtained by substituting $y(\xi)$ in the solution of the differential equation by the approximating function $\phi(x:\underline{b})$

CHAPTER III

Alphabetic

$a_m, \hat{a}_m$	mth coefficient of the polynomial approximating $c^n(x)$ and its least-squares estimate
$b_m, \hat{b}_m$	$Da \cdot a_m$ and its least-squares estimate
$b_m^{(0)}$	initial guess of b_m
$c(x)$	dimensionless measure of the composition of the reactant
c_i^*	noise-free observation of c at $x=x_i$
$\tilde{c}_i, \tilde{c}_{ij}$	noisy observation of c at $x=x_i$, for a certain run and for the jth run in specific

$\hat{c}_{k,ij}$	value of c at $x=x_i$, for the jth run, obtained by evaluating the corresponding approximating polynomial of degree k
$Da, \hat{Da}$	Damkohler number and its least-squares estimate
$\overline{Da}$	average of the individual least-squares estimates of Da
J	number of runs with a certain data set
K	optimum degree of the polynomial approximating c(x)
N	number of data points per run
$n, \hat{n}$	reaction order and its least-squares estimate
$\overline{n}$	average of the individual least-squares estimates of n
p	number of parameters estimated in Phase 2
$Pe, \hat{Pe}$	Peclet number and its least-squares estimate
$Pe^{(0)}$	initial guess of Pe
$\overline{Pe}$	average of the individual least-squares estimates of Pe
Q(c)	term accounting for the kinetics of decomposition
S, S_1, S_2	least-squares objective functions
$\hat{S}^2_{Da}, \hat{S}^2_{Pe}, \hat{S}^2_n$	individual least-squares estimates of the variances of Da, Pe, and n
$\tilde{S}^2_{Da}, \tilde{S}^2_{Pe}, \tilde{S}^2_n$	variance estimates of Da, Pe, and n, obtained from their least-squares estimates $\hat{Da}$, $\hat{Pe}$, and $\hat{n}$, using all runs
$\overline{S}^2_{Da}, \overline{S}^2_{Pe}, \overline{S}^2_n$	averages of $\hat{S}^2_{Da}$, $\hat{S}^2_{Pe}$, $\hat{S}^2_n$, using all runs
$S^2_{k,j}$	measure of the performance of polynomial of degree k, in approximating the observations in the jth run

$w(x), w_i$	continuous and discrete weighting factors, reflecting one's confidence in each individual observation

Greek

$\hat{\alpha}_m$	least-squares estimate of the mth coefficient of the Forsythe polynomial of degree m
$\varepsilon_{(x)}, \varepsilon_i, \varepsilon_i'$	continuous and discrete model errors
$\tilde{\varepsilon}_{ij}$	random number with Gaussian distribution and zero mean, used for generating noisy observations
ξ	dummy variable, used for integration
σ	standard deviation of the noise in the composition measurements
$\phi_m(x)$	Forsythe polynomial of degree m

CHAPTER IV

Alphabetic

A,B,C	reactants
a_1, a_3	functions of the unknown parameters, k_1, k_2, and k_3, defined by Equation (IV-19)
b_1, b_3	functions of the unknown parameters k_1, k_2, and k_3, defined by equation (IV-19)
$c_{1,0}, c_{1,1}, c_{1,2}$	linear coefficients in Equation (IV-81)
$c_{3,0}, c_{3,1}, c_{3,2}$	linear coefficients in Equation (IV-82)
$F_1(\underline{x}:\underline{k})$	function, defined by Equation (IV-52)
$F_3(\underline{x}:\underline{k})$	function, defined by Equation (IV-53)
K_1, K_2, K_3	equilibrium constants defined by Equation (IV-11)

k_{ij}	reaction rate constant for the decomposition of species i to species j; i,j=1,2,3, i≠j, $time^{-1}$
k_1, k_2, k_3	reaction rate constants defined by Equation (IV-12), $time^{-1}$
$k_1^{(0)}, k_2^{(0)}, k_3^{(0)}$	initial guesses of k_1, k_2, and k_3
$\hat{k}_1, \hat{k}_2, \hat{k}_3$	least-squares estimates of k_1, k_2, and k_3
$\bar{k}_1, \bar{k}_2, \bar{k}_3$	averages of the individual least-squares estimates of k_1, k_2, and k_3
L	optimum degree of polynomial P(t)
M	optimum degree of polynomial Q(t)
N	number of data points per run
P(t)	polynomial approximating the observations of x_1
$p_m, \hat{p}_m$	mth coefficient of P(t) and its least-squares estimate
Q(t)	polynomial approximating the observations of x_3
$q_m, \hat{q}_m$	mth coefficient of Q(t) and its least-squares estimate
R(t)	exponential function approximating the observations of x_1
r_0, r_1	linear coefficients of R(t)
S(t)	exponential function approximating the observations of x_3
s_0, s_1	linear coefficients of S(t)
S	least-squares objective function
$\hat{s}^2_{k_1}, \hat{s}^2_{k_2}, \hat{s}^2_{k_3}$	individual least-squares estimates of the variances of k_1, k_2, and k_3
$\tilde{s}^2_{k_1}, \tilde{s}^2_{k_2}, \tilde{s}^2_{k_3}$	variance estimates of k_1, k_2, and k_3, obtained from their least squares estimates k_1, k_2, and k_3, using all runs

$\bar{\hat{S}}^2_{k_1}, \bar{\hat{S}}^2_{k_2}, \bar{\hat{S}}^2_{k_3}$	averages of $\hat{S}^2_{k_1}$, $\hat{S}^2_{k_2}$, and $\hat{S}^2_{k_3}$ using all runs
t	measure of time
$v_1, v_1^{(0)}$	exponential coefficient of R(t) and its initial guess
$v_3, v_3^{(0)}$	exponential coefficient of S(t) and its initial guess
$\underline{W}$	2N x 2N diagonal weighting matrix for the observations of x_1 and x_3
$\underline{W}_1$	NxN diagonal weighting matrix for the observation of x_1
$\underline{W}_3$	NxN diagonal weighting matrix for the observation of x_3
x_1, x_2, x_3	normalized measures of the compositions of A, B, and C
$x_{1,0}, x_{2,0}, x_{3,0}$	values of x_1, x_2, and x_3 at t=0
$x_{1,e}, x_{3,e}$	equilibrium values of x_1 and x_3
$x^*_{1,i}, x^*_{3,i}$	noise-free observations of x_1 and x_3 at $t=t_i$
$\tilde{x}_{1,i}, \tilde{x}_{3,i}$	using observations of x_1 and x_3 at $t=t_i$, for a certain run
$\tilde{x}_{1,ij}, \tilde{x}_{3,ij}$	using observations of x_1 and x_3 at $t=t_i$, for the jth run in specific

Greek

$\varepsilon_1(t), \varepsilon_3(t)$	continuous model errors
$\varepsilon_{1,i}, \varepsilon_{3,i}$	discrete model errors
$\tilde{\varepsilon}_{ij}, \tilde{\varepsilon}'_{ij}$	random numbers with Gaussian distribution and zero mean, used for generating noisy observations

λ_1, λ_3	exponential coefficients in Equations (IV-81) and (IV-82)
ξ	dummy variable, used for integration
σ_1, σ_3	standard deviations of the noise in the observations of x_1 and x_3

CHAPTER V

Alphabetic

A	reactant
A'	cross-sectional area of tube, sq. ft.
a_1, a_2	unknown parameters
$a_1^{(0)}, a_2^{(0)}$	initial guesses of a_1 and a_2
$\hat{a}_1, \hat{a}_2$	least-squares estimates of a_1 and a_2
$\bar{a}_1, \bar{a}_2$	averages of the individual least-squares estimates of a_1, and a_2
B,C	products
$c_{p_A}, c_{p_B}, c_{p_C}$	heat capacities of the reactant and products, BTU/lbmole-°R
D	constant, defined by Equation (V-11)
D_i	inside diameter of tube, ft.
$f(T,z:a_2)$	function, defined by Equation (V-17)
k	overall reaction rate term, sec^{-1}
k_1, k_2	linear and exponential coefficients in the overall reaction rate term
L	optimum degree of polynomial P(x)
M	optimum degree of polynomial R(x)
N	number of data points per run

n_0	feed rate of A, lbmoles/hr.
P	mean pressure inside the reactor, psia
$\hat{p}_m$	mth coefficient of P(x)
q	heat input from furnace, BTU/hr-ft of tube
R	ideal gas constant, 10.73 psia-cu. ft/lbmole-°R
R(x)	polynomial approximating the temperature observation
$\hat{r}_m$	mth coefficient of R(x)
S	least-squares objective function
$\hat{S}^2_{a_1}, \hat{S}^2_{a_2}$	individual least-squares estimates of the variances of a_1 and a_2
$\tilde{S}^2_{a_1}, \tilde{S}^2_{a_2}$	variance estimates of a_1 and a_2, obtained from their least-squares estimates $\hat{a}_1$ and $\hat{a}_2$, using all runs
$\bar{S}^2_{a_1}, \bar{S}^2_{a_2}$	averages of $\tilde{S}^2_{a_1}$ and $\tilde{S}^2_{a_2}$, using all runs
T, T_R	measure of temperature, °R
T_K	measure of temperature, °K
$T_0, T_{R,0}$	value of T at x=0
T_i^*	noise-free observation of T at $x=x_i$
$\tilde{T}_i, \tilde{T}_{ij}$	noisy observation of T at $x=x_i$, for a certain run and for the jth fun in specific
$\underline{W}$	2N x 2N diagonal weighting matrix for the temperature and conversion observations
$\underline{W}_z$	NxN diagonal weighting matrix for the conversion observations

$\underline{W}_T$	NxN diagonal weighting matrix for the temperature observations
x	measure of the distance from the reactor inlet, ft.
z	measure of the fractional conversion of A to B and C
z_0	value of z at x=0
z_i^*	noise-free observation of z at $x=x_i$
$\tilde{z}_i, \tilde{z}_{ij}$	noisy observation of z at $x=x_i$, for a certain run and for the jth run in specific

Greek

ΔH_R	heat of reaction, BTU/lbmole
$\varepsilon_{z,i}, \varepsilon_{T,i}$	discrete model errors
$\tilde{\varepsilon}_{z,ij}, \tilde{\varepsilon}_{T,ij}$	random numbers with Gaussian distribution and zero means, used for generating noisy conversion and temperature observations
σ_z, σ_T	standard deviations of the noise in the conversion and temperature observations
$\phi(x:a_2)$	function, defined by Equation (V-19)
$\psi(x:a_1,a_2)$	function, defined by Equation (V-20)

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APPENDIX

A BRIEF OUTLINE OF THE NONLINEAR LEAST-SQUARES METHOD FOR PARAMETER ESTIMATION

Given a model of the form:

$$y = g(x:\underline{a}) \tag{A-1}$$

and a set of observations $\{y_i, x_i;\ i=1,2,\ldots,N\}$, the estimation of the p-dimensional parameter vector $\underline{a}$ is desired. This is accomplished by minimizing:

$$S = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} [y_i - g(x_i:\underline{a})]^2 \tag{A-2}$$

Starting with an initial set of parameter guesses, $\underline{a}_0$, the solution for the vector of corrections to the parameter guesses is given by:

$$\underline{\delta}_0 = (\underline{G}_0^T \underline{G}_0)^{-1} \underline{G}_0^T \underline{\varepsilon}_0 = \underline{R}_0^{-1} \underline{v}_0 \tag{A-3}$$

where $\underline{G}_0$ = Nxp matrix of sensitivity coefficients,

$\underline{\varepsilon}_0 = \tilde{\underline{y}} - \hat{\underline{y}}_0$,

$\hat{\underline{y}}_0$ = N-vector of predicted values of y by the algorithm

$\underline{\delta}_0$ = p-vector of corrections to the parameter guesses.

In Equation (A-3), T stands for transpose. The improved set of parameters is obtained using:

$$\underline{\delta}_1 = \underline{a}_0 + \underline{\delta}_0 \tag{A-4}$$

The above procedure is repeated until every element of $\underline{\delta}$ is smaller than a predetermined error criterion. After this objective has been reached, the variance-covariance matrix of parameters, $\underline{C}$, is obtained from:

$$\underline{C} = \sigma_\varepsilon^2 \, \underline{R}^{-1} \tag{A-5}$$

where σ_ε^2 is the variance of the observation errors. In cases where an estimate of its value is not available, it can be approximated by:

$$\sigma_\varepsilon^2 \simeq \frac{\sum_{i=1}^{N} [\tilde{y}_i - g(x_i : \hat{\underline{a}})]^2}{N - p} \tag{A-6}$$

where $\hat{\underline{a}}$ is the vector of the least-squares estimates of $\underline{a}$, obtained with the algorithm outlined above.

In cases where more than one dependent variable is observed, weights should be included in the analysis in order to express one's confidence in the observed values of the different variables. This is done in the following manner:

$$\underline{\delta} = (\underline{G}^T \underline{W} \underline{G})^{-1} \underline{G}^T \underline{W} \underline{\varepsilon} \qquad \text{(A-7)}$$

where, this time $\underline{G}$ = Mxp matrix of sensitivity coefficient,

$\underline{\varepsilon}$ = M-vector residuals,

M = NxK,

K = number of dependent variables observed,

$$\underline{W} = \begin{bmatrix} \underline{W}_1 & \underline{0} & \cdots & \underline{0} \\ \underline{0} & \underline{W}_2 & \cdots & \underline{0} \\ \vdots & & \ddots & \vdots \\ \underline{0} & & & \underline{W}_K \end{bmatrix} \qquad \text{(A-8)}$$

$$\underline{W}_K = \frac{1}{\sigma_K^2} \underline{I}; \quad k=1,2,\ldots,K \qquad \text{(A-9)}$$

$\underline{I}$ = NxN identity matrix,

σ_K^2 = variance of the observation errors for the kth dependent variable.

The diagonality of $\underline{W}$ follows from the assumption that observations of different variables are uncorrelated.